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PRELIMINARY ASSESSMENT OF AIR EMISSIONS FROM AERATED WASTE TREATMENT SYSTEMS AT HAZARDOUS WASTE TREATMENT STORAGE AND DISPOSAL FACILITIES

by

C. C. Allen, D. A. Green
J. B. White and J. B. Coburn
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

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Project Officer

Ronald J. Turner
Thermal Destruction Branch
Alternative Technologies Division

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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Methods for estimating emissions resulting from mass transfer of volatile organic compounds from dilute wastewaters into air are reviewed and applied to full-scale and pilot-scale treatment systems.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report presents and evaluates kinetic and predictive methods for estimating volatile organic compound emissions from aerated wastewater treatment processes. The available theoretical and semiempirical models were used to predict emissions within limits of ± 20 percent in the absence of competing removal mechanisms. Five general treatment plant configurations are described in this study: trickling filtration, activated sludge (mechanical aeration), activated sludge (diffused aeration), activated sludge-aerated lagoons (mechanical aeration), spray ponds (mechanical spray). The results should be of interest to regulatory agencies, industrial, and other sources involved in VOC emissions control.

Requests for further information regarding this study should be directed to the Project Officer at the Hazardous Waste Engineering Research Laboratory, Cincinnati.

Thomas R. Hauser
Director
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio

ABSTRACT

Aerated wastewater treatment unit operations are used for the removal of organic compounds from hazardous waste and other industrial wastewater streams. In some operations, aeration is required to supply oxygen for aerobic decomposition of organics; in other operations, air/water contact occurs as the wind blows across the surface of the ponded or flowing wastewater. Methods for estimating emissions resulting from air stripping of volatile organic compounds that can accompany aerated treatment are reviewed and applied to full scale and pilot plant wastewater treatment plants.

Typical treatment plants which may be used for aerated treatment of industrial waste are provided for systems employing trickling filters, activated sludge and aerated lagoons. The size and configuration of actual treatment plants are highly variable, corresponding to the highly variable volume and strength of industrial wastewater. Typical size and residence time specifications for unit operations within these plants are included.

The recommended mathematical models are used to generate predictions of the fate of volatile organic compounds in wastewater treatment systems. Where full scale plant data are available, predictions generally agree with measurements (within the limits of accuracy which result from variations in sampling and chemical analysis). For this reason, the mathematical models can be used to estimate emissions for those systems where no field data are available.

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SECTION 1

INTRODUCTION AND OBJECTIVES

Under the 1976 Resource Conservation and Recovery Act (RCRA) the EPA Office of Air Quality Planning and Standards (OAQPS) is developing regulations to control air emissions from hazardous waste treatment, storage, and disposal facilities (TSDF). The purpose of the air emissions regulations is to protect human health and the environment from emissions of volatile organic compounds (VOCs), particulates, and aerosols.

The sources of TSDF emissions include storage tanks, treatment processes, surface impoundments, lagoons, landfills, land treatment, and drum storage and handling facilities. Those processes involving the use of air (biological treatment and cooling) or subject to the introduction of air (stirred equalization and neutralization) may emit VOC as a consequence of air stripping.

In order to further understand and better estimate the source and extent of VOC emissions from TSDFs, model aerated treatment facilities are investigated. Various mathematical models are presented to predict the role and extent of VOC emissions during each of the different process conditions encountered. The models include a methodology for estimating the relative importance of competing removal pathways (i.e., adsorption and biological oxidation). The study is limited to those biological processes and physical chemical processes with potential to vent VOC to the air.

The basic problem in evaluating air emissions from aerated waste treatment processes is to determine the importance of competing mechanisms. In an activated sludge biological treatment process, for example, the major mechanisms for removal of dissolved contaminants from the aqueous waste are biological oxidation, adsorption on biomass, and mass transfer into the air. In a rough analysis of "removal efficiency", concentrations of the contaminant in the aqueous influent and effluent are measured and the fraction of the contaminant which disappears in the process is reported as an efficiency. This procedure gives no information about the relative importance of competing removal mechanisms.

Where one or more of the removal mechanisms is destructive of the contaminant, e.g., chemical or biological oxidation, and other mechanisms, e.g., air stripping or aerosol dispersal, are nondestructive, measurements of the relative importance of the competing mechanisms become complicated. In such a case, the contaminant removed by the non-destructive mechanism must be recovered and the balance assumed to have been destroyed. Errors in chemical analyses, and particularly sampling errors, will have a great impact on calculations of the fraction of the contaminant which has been destroyed.

Alternatively, data may be obtained under controlled laboratory conditions and adapted to provide reasonable estimates of emissions expected under field conditions. One way to do this is to conduct experiments in covered vessels to permit accurate sampling of vent gases and accurate metering of vent gas flow rates. Another approach involves inhibiting the destructive removal mechanisms by taking steps to chemically sterilize the system or to substitute an inert gas such as nitrogen for air. In the latter approach, the mass transfer to the gas phase will continue to occur, eliminating all of the destructive mechanisms. The elimination of the destructive mechanisms may cause a higher concentration and inflate mass transfer. This effect can be accounted for in the data analysis. Influent and effluent aqueous phase sampling can be used to determine the extent of removal resulting from stripping. Vapor phase sampling of such a laboratory system should close the mass balance for the system. The extent to which under-recovery or over-recovery of contaminants is found can be used to evaluate the adequacy of laboratory vapor phase sampling techniques.

When adsorption is unimportant (typically true with VOCs), then any difference between influent and effluent contaminant levels may be attributed to air stripping and biological oxidation. Thus, if a rate expression describing mass transfer through air stripping is available, it can be used to calculate contaminant levels which are susceptible to destructive removal mechanisms. Conversely, if rate data for the destructive removal mechanisms (e.g., biological oxidation kinetics) are available, these can be used to estimate the relative importance of air stripping.

One approach to the problem described above is to measure the total disappearance in the field and then apply mathematical models obtained from laboratory data to simultaneously estimate the rate of stripping and biological oxidation. When these models account for significantly more or significantly less contaminant removal than the observed total removal, several steps can be taken. The simplest method is to assume that the mass transfer model is more accurate than the biological oxidation model and account for biological oxidation (and other destructive removal mechanisms) by difference. The mass transfer models are in fact more accurate predictors than the biological oxidation models because they are less affected by changes in operating conditions and influent wastewater composition and thus are less site-specific. In some cases, air sampling programs must be conducted to verify the prediction of stripping models. The interpretation of data obtained under field conditions is subject to considerable error.

The objectives of this study are to present and evaluate the various kinetic and predictive fate models that are applicable to aerated wastewater treatment systems. Four different waste treatment systems are considered. These are (1) trickling filters, (2) activated sludge, (3) aerated lagoons, and (4) spray ponds. When possible, model predictions are compared with experimental data.

The approach taken is to investigate mathematical models and correlations available in the literature for mass transfer in systems similar to wastewater treatment units. Classical engineering approaches to mass transfer in strippers and absorbers, packed bed design, and stream and lake reaeration are considered and adapted as necessary to wastewater treatment systems.

SECTION 2

SUMMARY AND CONCLUSIONS

The available theoretical and semiempirical methods for predicting the rates of mass transfer of volatile organic compounds from dilute solution into air can be used to accurately (± 20%) predict emissions from aerated wastewater treatment processes in the absence of competing removal mechanisms. Where liquid phase concentration data and system operating conditions are well characterized, VOC emissions from aerated lagoons, activated sludge processes, trickling filters, and clarifiers associated with wastewater treatment systems can be estimated within the accuracy of sampling and chemical analysis results.

The presence of competing removal mechanisms, the most important of which is bioxidation, reduces the accuracy of emissions predictions based on plant influent concentration data because direct mass balances cannot be obtained. If bulk wastewater concentrations are known for individual treatment units, then reasonably accurate (± 20%) predictions of the fate of VOCs can be made. However, when only the concentration of the influent to the entire plant is known, accurate rate data for biooxidation becomes more important and the absence of this data has a greater influence on the accuracy of emissions estimation (uncertainties of ± 50% may result).

Biooxidation rate data is available in the literature for various organic compounds which may be present in industrial wastewater. The data are highly dependent on the experimental conditions under which they are obtained and are not easily adapted to real systems which may have different initial concentrations, biomass loadings, nutrient and inhibitor concentrations, etc. A table of bioxidation rate data obtained from the literature has been included in Section 4 to provide a starting point for calculations.

Industrial waste treatment systems vary widely in design, reflecting the wide variation in the waste streams to be treated. The recommended predictive mathematical models are adaptable to widely varying volumetric flow rates. Residence time, which in actual process system designs accounts for the concentration and increases with the difficulty of removal of organic compounds and suspended solids, must be specified from actual system designs or estimated (less accurately) from removal rate data. Model plant designs have been developed in this study which fit within the wide range of suitable designs.

The best mathematical models, as determined in this study, have been compared with experimental measurements of full-scale and pilot-scale wastewater treatment systems. Sample calculations are included in **Appendix B.**

The study concluded that reliable emissions estimates (i.e., estimates within the accuracy which is expected to result from variations in sampling and chemical analysis) can be made using selected mathematical models and correlations. Where plant operating conditions including residence times, aeration rates, dimensions, etc., are available, limitations in applying the mathematical models result from lack of accurate biooxidation and partition coefficient data. When descriptions of specific plant operating parameters are not available, rough estimates can be made based on model plant designs, adjusted for wastewater flow rates.

SECTION 3

DESCRIPTION OF AERATED WASTEWATER TREATMENT PROCESSES

INTRODUCTION

Aerated wastewater treatment systems are primarily designed to promote decomposition of organic contaminants by aerobic organisms. Complete decomposition of hydrocarbons is accomplished by oxidation to carbon dioxide and water. Intermediate steps in this oxidation process may result in the conversion of larger organic molecules to smaller organic molecules. Organic nitrogen and phosphorus present are ultimately converted to nitrate and phosphate. A portion of the carbon, nitrogen, and phosphorus removed from the wastewater is converted into additional organisms.

Only oxygen which is dissolved in the wastewater is available for use in the reaction. At common treatment temperatures, under air at one atmosphere pressure the solubility of oxygen in the wastewater is limited to approximately 5 to 10 mg/L. Oxygen must be transferred into the wastewater on a continuous basis to replace that used in the oxidation reactions. A variety of processes have been developed by environmental engineers to promote the oxidation reactions and supply oxygen to the wastewater. From an engineering standpoint, these processes differ with respect to the environment of the oxidizing organisms and the means of oxygen transfer.

Aerobic biological oxidation processes include variations of the activated sludge process, trickling filters and aerated lagoons. In addition, because the dissolved air flotation process involves aeration of wastewater for separation of solids, biological oxidation may take place simultaneously with solids separation but this does not influence process design. Wastewater treatment systems include other process units which are not aerated but permit air/water contact which can result in transfer of volatile chemicals out of the wastewater. These process units include both turbulent and quiescent contact over a range of liquid residence times.

All municipal wastewater treatment plants and some industrial wastewater treatment plants have a bar screen or an equivalent device to remove large solids (>0.5 cm) from the influent wastewater. Typically wastewater flows at approximately 0.5 m/sec through a screen of vertical metal bars spaced approximately 0.5 cm apart. The turbulence resulting from this screening promotes air-water contact and potential emissions of volatile material may result. Although the amount of air-water contact is limited at this point (due to the short residence time) the influence of mass transfer is increased because the bar screen occurs at the beginning of the treatment process. For extremely volatile contaminants a significant fraction of the total concentration may volatilize at the first opportunity.

Grit chambers are process units designed for removal of dense solids (e.g., sand) by sedimentation. Their purpose is to simplify further treatment processes. A very short residence time is sufficient for grit removal. For the purposes of this report, bar screens and grit chambers have been lumped together as "pretreatment" and are considered to operate in plug flow.

Industrial waste treatment plants designed to treat wastewater that is variable in contaminant concentration may include an equalization tank. The purpose of using such a process unit is to avoid shocking the biological treatment systems with intermittent high concentration waste loads. Typically, the equalization tank is a large open tank with sufficient volume to smooth out variations in influent concentration. The tank may be agitated mechanically to promote mixing. Volatilization of contaminants may occur in such a unit as a result of either normal evaporation or the agitation.

Wastes that are strongly acidic or basic may be neutralized to promote biodegradation. Neutralization may take place in an open agitated mixing tank with the addition of base or acid. Emissions from this process unit will be similar to those from an agitated equalization basin.

Process units designed for gravity separation of suspended solids are ordinarily designed to minimize agitation to prevent resuspension of solids. These clarifiers and sedimentation tanks provide a large surface area for evaporation of volatiles and may be designed for several hours of residence time. In some plant designs, sedimentation tanks may be placed before or after biological treatment units: before, for the removal of solids present in the influent waste stream, and after, for separation of biomass flocs. If a high degree of volatile compound removal is achieved (either through biooxidation or volatilization) in the biological oxidation units, emissions from the secondary clarifiers (i.e, those designed to separate biomass from treated effluent) will be relatively unimportant.

Aerated treatment units specifically designed for biological treatment of contaminants in wastewater have the greatest potential for emission of volatiles because of the extent of air/water contact and the length of residence times provided. Such units include roughing filters, trickling filters, activated sludge units and aerated lagoons. Several different methods of aeration are available for activated sludge units and aerated lagoons.

The activated sludge process consists of an aeration tank in which wastewater is contacted with microorganisms. The nature of the aeration system promotes mixing, and as an approximation, the aeration tank can be considered a completely mixed reactor. The microorganisms responsible for oxidation of wastewater components are present in the form of flocs of biomass. These flocs are suspended in the aeration tank and are continually agitated by the aeration system. The oxidation of the wastewater components results in the conversion of hydrocarbons to carbon dioxide and water. In addition, new biomass is formed from a portion of the wastewater components. Biomass flocs leave the aeration tank along with the treated effluent and are typically separated from the effluent by gravity sedimentation in secondary clarifiers. Commonly, some fraction of the separated biomass (sludge) is returned to the aeration tank (return sludge) to maintain or increase the number of microorganisms available for oxidation of the organic material in the wastewater. The remainder (waste sludge) is removed from the system, dewatered and disposed of as solid waste. The dewatering of the waste sludge is important for volume reduction; the separated liquid portion is returned to the treatment plant. Some minor VOC emissions are possible in this solid separation process (e.g., in centrifuging or in filtering the waste).

Oxygen must be continuously supplied to the wastewater in the aeration tank by mass transfer from air to the liquid phase. This is generally accomplished using either submerged aerators or surface aerators. Submerged aerators operate through the discharge of air through diffusers near the bottom of the aeration tank. The oxygen transfer occurs as the air bubbles rise to the surface of the tank. Volatile components may diffuse into the air bubbles as they rise and be released at the surface. Bubble size may vary with smaller bubbles resulting in a greater degree of oxygen transfer to the wastewater, as well as a more efficient stripping of organics. Smaller bubbles cost more to produce because of is the increased compressor horsepower required by the diffusers.

Surface aerators promote transfer of oxygen into the wastewater through vigorous agitation of the surface of the aeration tank. Typically, a rapidly rotating partially submerged impeller is used to create a large amount of turbulence in the wastewater at the top of the aeration tank. The wastewater in the vicinity of the impeller is rapidly saturated with oxygen and a high degree of mixing circulates this saturated water throughout the volume of the tank. Activated sludge units typically operate as very nearly completely mixed systems whether equipped with diffused or surface aerators.

Trickling filters promote biological oxidation of wastewater components by microorganisms in the form of a slime layer supported on a coarse filter medium. Wastewater is sprayed or trickled over a bed of crushed rock (particle size is approximately 5 cm) up to approximately 3 m deep. The sprayer is usually a rotating arm with nozzles spaced along its length. The arm slowly rotates over the (generally circular) filter bed at a height of approximately 20 cm. The media is continuously wetted with wastewater and a layer of biomass accumulates on the surface of the rocks. In some cases, specially designed plastic filter media have been used as a support for the biomass. Oxygen is supplied by transfer from the ambient air (the pores between the coarse media are filled almost entirely with air with the exception of a thin film of wetted biomass on the surface of the media). Air flows through the filter, induced by a thermal density gradient, at a rate sufficient to prevent oxygen depletion. This air velocity can vary widely (as well as change directions), due to weather conditions but is typically on the order of 15 cm/sec.

Biomass loading on trickling filters eventually reaches a steady state. Additional biomass produced is roughly equivalent to that which sloughs off and leaves the filter with the treated effluent. This biomass is removed in a secondary clarifier prior to discharge. A much lower mass is produced in trickling filters than in the activated sludge process.

Operation of aerated lagoons is similar to that of activated sludge units in that both are well mixed (completely mixed as a first approximation) systems with the microorganisms responsible for biological oxidation suspended in the wastewater. A consequence of the high degree of mixing is that the bulk concentration approximates that of the effluent concentration. Typically, aeration is supplied with either surface aerators or diffused aeration systems similar to those of the activated sludge process. The distinction between activated sludge processes and aerated lagoon processes is not precise.

A type of aerated lagoon referred to as a spray pond is aerated by pumping a portion of the wastewater through a spray nozzle into the air. As the droplets rise and fall back into the spray pond they absorb oxygen which is distributed throughout the bulk wastewater by diffusion and dispersion. The degree of mixing provided by systems of this type is somewhat less than that provided by diffused or surface mechanical aerators, and some regions of the pond may be relatively stagnant and lower in dissolved oxygen concentration than the bulk wastewater. Aerosol formation and wind loss (of liquid droplets as opposed to evaporation losses) may be important removal mechanisms for spray pond systems.

DESCRIPTION OF INDUSTRIAL PROCESSES

Most municipal wastewater treatment systems in the United States include aerated biological oxidation processes for removal of biochemical oxygen demand from wastewater. Many municipal wastewater treatment plants accept untreated or partially treated industrial wastewater; in some cases, this wastewater may contribute more than 50% of the total flow through the treatment system. Industrial wastewater treatment plants commonly employ aerated biological waste treatment processes for removal of biodegradable wastewater components. For wastes which are amenable to treatment processes of this type, aerobic biological treatment methods are preferred to physical chemical treatment methods for reasons of cost. Process effluents which contain valuable byproducts or unreacted materials would first be subjected to recovery processes; the dilute effluent from the recovery processes would then be subjected to biological oxidation.

A study by SCS Engineers (1979) found that industrial wastes suitable for biological treatment are primarily produced by five major industries. These industries are petroleum refining, organic chemicals manufacturing, pulp and paper, iron and steel (coal conversion processes are included in this category because of the importance of coke manufacturing as a source of wastewater) and textile manufacturing. Extensive studies of water pollution and water reuse possibilities in these industries have been sponsored by EPA. Additional industrial wastewater sources are less important in terms of total volume produced but may represent important individual sites for emissions of volatile organic compounds during wastewater treatment processes.

Petroleum Refining

Wastewater production from petroleum refining was studied for the development of effluent guidelines (U.S. EPA, 1974a). Raw wastewater volumes and compositions were determined for individual plant sectors. In general, the wastewaters are contaminated with oil fractions including the crude oil input to the refinery and various refined products. Other organic contaminants present in the combined plant effluent include alcohols, phenols, and aromatics (benzene, toluene, xylene, etc.). Individual components of the highly complex crude oil and product fractions may result in varying levels of paraffins, olefins, naphthenes and polynuclear aromatic hydrocarbons dissolved or suspended in the wastewater.

Pretreatment of wastewater involves separation of suspended oil droplets and suspended solids using clarifiers or dissolved air flotation. Aerated biological treatment can involve aerated lagoons, activated sludge units, trickling filters, or cooling towers which are operated with biomass on the tower packing. Where land is readily available, large shallow oxidation ponds may be used (with very long residence times) without aeration equipment. Influent biochemical oxidation demand is typically lowered by 75 to 95% using aerated lagoons, 80 to 90% using activated sludge and 60 to 85% using trickling filters (U.S. EPA, 1974a). The effluent guidelines document gives no estimate of the fraction of removal due to stripping.

The influent wastewater to activated sludge units and aerated lagoons is reported by EPA to contain up to 40 mg/L of phenols and up to 200 mg/L of BOD under typical conditions. Refinery process upsets or partial shutdowns can result in either much higher or much lower influent concentrations. In addition, failure or upsets in upstream wastewater pretreatment equipment such as clarifiers and oil separators can increase the BOD of the influent to the aeration units. Waste biomass is produced in the activated sludge and trickling filter processes. Water associated with this sludge is typically separated and returned to the treatment system. The dewatered sludges may contain organic compounds of both low volatility and low biodegradability which may eventually volatilize to some extent if applied to land as a final disposal technique.

Rosenburg, et al. (1976) surveyed hazardous waste production and management in the refinery industry. Waste sludge from activated sludge, trickling filters, and aerated lagoons was found to contain between 1.7 and 10.2 mg phenols per kg dry solids. The benzo-a-pyrene content of this material ranged between 0.002 and 0.005 mg/kg dry solids. At present the waste sludge is typically disposed of by landfilling or land spreading.

The 1979 EPA effluent guidelines survey (EPA 440-1-74-014a) for petroleum refineries covered 309 plants, which included (as of 1976), 68 dissolved air flotation systems, 50 activated sludge systems, 10 trickling filter systems, and 73 aerated lagoon systems were in service. A list of organic priority pollutants from the 1982 Effluent Guideline Survey (EPA-440/1-82-014) and the maximum levels observed is given in Table 1.

Organic Chemical Industry

The 1975 EPA effluent guidelines study of the organic chemical industry covered a total of 98 wastewater treatment and disposal facilities. Among the aerated waste processes in use, the study identified activated sludge systems, aerated lagoons, and trickling filters. Of the 98 facilities, 28 discharged to municipal treatment plants, with or without some degree of pretreatment.

The composition and concentration of wastewater subjected to aerated treatment processes varies widely depending upon the products manufactured and production processes in use. Wastewater production ranged from 0.05 m^3 wastewater per ton of chlorobenzene produced by chlorination of benzene to 121 m^3 wastewater per ton of chlorotoluene produced by chlorination of toluene for the processes investigated in the 1975 EPA study. The biochemical oxygen demands of the wastewater ranged from 3 mg/L for production of propylene glycol by hydrolysis of propylene oxide to 303,000 mg/L for production of cresol by methylation of phenol.

Erickson et al. (1980) estimated uncontrolled secondary emissions from treatment of wastewater from organic chemical manufacturing at 650 g of volatile organic emissions per ton of product. Based on total synthetic organic chemical production of 10^8 Mg in 1978, the estimated air emissions from waste-

TABLE 1. ORGANIC PRIORITY POLLUTANTS DETECTED IN REFINERY DISCHARGES AT MORE THAN ONE LOCATION*

Compound	Maximum Concentration μg/L
chlorobenzene	31
chloroform	100
1,1 dichloroethane	54
ethylbenzene	18,000
toluene	48,000
2,4 dimethylphenol	18,300
2,4 dinitrophenol	11,000
phenol	33,500
acenaphthene	665
anthracene	1750
butyl benzyl phthalate	16
4 chlorophenyl phenyl ether	30
chrysene	30
diethylphthalate	38
fluoranthene	812
naphthalene	3750
pyrene	16
fluorene	495
isophorone	3550
phenanthrene	1750

*Pesticides excluded

SOURCE: Effluent Guidelines, EPA-440/1-82-014 water treatment are 6.5 x 10^4 Mg/year. These estimates were based on a model plant which consisted of a 3 m deep clarifier and an activated sludge system with a retention time of three hours.

Iron and Steel Industry

The EPA effluent guidelines study of the iron and steel industry (1982) covered options for suspended solids removal, oil and grease removal, dissolved metal removal, and organic chemical removal from aqueous waste streams. The greatest opportunities for emissions of VOCs occur in the organic removal processes. Biological oxidation systems (typically activated sludge systems) were in use at eighteen coke-making operations. Well operated activated sludge systems were found to remove more than 90% of toxic organics and nearly 100% of phenolics, naphthalene and xylene. No data were provided on possible air emissions from those processes. The average concentration in the effluent from one individual biological treatment system treating byproduct coke manufacturing wastewater was 3 ppb phenol, < 0.05 ppb naphthalene, 2 ppb benzo(a)-pyrene and < 0.05 ppb benzene. These low concentrations may reflect stripping and adsorption losses as well as biooxidation. EPA estimates of achievable concentrations in the effluent from two stage activated sludge systems are given in Table 2.

Suspended solids removal techniques in use in the iron and steel industry include settling basins of up to 400 acres surface area, but the typical size range is between 0.01 and 10 acres for the 140 settling basins found at 39 steel plants. Settling basin retention times are on the order of days. Conventional clarifiers are also used for suspended solids removal with shorter residence times (hours instead of days) than settling basins.

Textile Industry

An EPA technology transfer report (EPA-625/3-74-004) on the textile industry covered cotton, wool, and synthetic fiber processing. Cotton mills discharge between 170 and 580 gallons of wastewater per kg of finished product. The wastewater BOD ranges between 175 and 800 mg/L. Large variations in waste volume and composition occur from day to day due to batch process operations. Suspended solids can range up to 100 mg/L. Cotton processing wastewater contains fine suspended fibers which are difficult to remove in primary clarifiers, and consequently, these fibers are present in the aeration basin.

TABLE 2. TOXIC ORGANIC CONCENTRATIONS ACHIEVABLE BY TWO STAGE ACTIVATED SLUDGE SYSTEM

Priority Pollutant	Achievable Concentration (ppb)
	Biological Oxidation
*Acrylonitrile	100
*Benzene	50
*2,4,6-Trichlorophenol	50
*Chloroform	200
*2-Chlorophenol	50
*2,4-Dimethylphenol	5
*2,4-Dinitrotoluene	50
*2,6-Dinitrotoluene	100
Ethylbenzene	25
*Fluoranthene	5
Isophorone	100
*Naphthalene	5
2-Nitrophenol	100
*4,6-Dinitro-o-cresol	25
*Phenol	25
*Phthalates, Total	200
*Benzo(a)anthracene	5
*Benzo(a)pyrene	5
*Chrysene	10
Acenaphthylene	10
Anthracene	1
Fluorene	5
Pyrene	10
*Tetrachlorethylene	100
*Toluene	50
Xylene	100

Source: Development Document for Effluent Limitations Guidelines and Standards for the Iron and Steel Point Source Category, EPA 440/1-82/024 (May 1982).

*Indicates Appendix VIII compounds (40CFR261).

Wool processing mills discharge approximately 170 gallons of wastewater per kg of finished product if unscoured wool (i.e., wool which contains natural grease and other impurities) is used as the starting material. This wastewater has between 900 and 3000 mg/L BOD and approximately 100 mg/L suspended solids.

Synthetic fiber processing (i.e., scouring, dyeing and finishing but not production of the fibers) wastewaters vary greatly in volume and composition depending on the type of fiber (e.g., nylon, acrylic, polyester, etc.) and the type of processing. Organic chemicals removed from the fibers during scouring and dyeing or scouring and bleaching operations include sulfonated oils from acetate, esters from nylon, formic acid and aromatic amines from acrilics. Dyeing operations produce wastewater which can contain chlorobenzenes and phenolic compounds. Much of the organic content of dyeing wastewater is, by design, non-biodegradable or very slowly biodegradable. Trickling filters are reported to remove 40-85% of the five day BOD from cotton and synthetic finishing wastewater (Porter, 1971). The biodegradable portion of the organic loading may be only a fraction of the total organic loading. BOD removals for activated sludge units are estimated at 70-95 percent and for aerated lagoons at 50-95 percent (Porter, 1971). For wool processing plants similar figures are given for trickling filters (80-85 percent) and activated sludge units (85-90 percent). A list of organic priority pollutants found in textile wastewater is given in Table 3.

Pulp and Paper Industry

Wastewater volume and composition from pulp and paper production varies with the type of process used and the end product. These wastewater streams have been found to contain organic sulfur compounds, phenolic compounds, and oils (SCS, 1979). A typical integrated pulp and paper mill using the bleached kraft process produces a total of 340 L of wastewater per Mg of paper produced (EPA Effluent Guidelines, 1976). Raw wastewater from the different categories of production using the bleached kraft process contains 240 mg/L BOD on average. A list of organic chemicals found in pulp and paper manufacturing wastewater is given in Table 4.

Pulp and paper manufacturing wastewater is subjected to pretreatment (i.e., bar screens) prior to primary clarification. Effluent guidelines assume 75 to 85 percent suspended solids removal with an overflow rate of 24 m^3/m^2-day. BOD removal is typically accomplished using aerated stabilization basins, which involve long residence times (e.g., 14 days) and are not well

TABLE 3. PRIORITY POLLUTANTS DETECTED IN RAW WASTEWATER FROM TEXTILE MANUFACTURING AT MORE THAN ONE LOCATION

Compound	Maximum concentration µg/L
acenaphthene	273
acrylonitrile	1,600
benzene	200
chlorobenzene	296
1,2,4 trichlorobenzene	14,000
hexachlorobenzene	2
1,2 dichloroethane	6
1,1,1 trichloroethane	1,200
1,1 dichloroethane	14
1,1,2,2 tetrachloroethane	21
2,4,6 trichlorophenol	94
para chlorometa cresol	29
chloroform	642
2 chlorophenol	131
1,2 dichlorobenzene	460
1,3 dichlorobenzene	1,700
1,4 dichlorobenzene	760
1,1 dichloroethylene	84
1,2 trans dichloroethylene	360
2,4 dichlorophenol	41
1,2 dichloropropane	100
2,4 dimethylphenol	190
ethylbenzene	19,000
methylene chloride	2,600
trichlorofluoromethane	45
naphthalene	2,079
4-nitrophenol	240
N-nitrosodiphenylamine	130
pentachlorophenol	310
phenol	4,930
bis 2 ethyl hexyl phthalate	1,450
butyl benzl phlthalate	160
di-N butylphthalate	67
di-N octylphthalate	10
diethyl phthalate	150
dimethyl phthalate	111
anthracene	12
fluorene	15
phenanthrene	12
tetrachloroethylene	1,130
toluene	3,200
trichloroethylene	5,600

TABLE 4. ORGANIC COMPOUNDS PRESENT IN WASTEWATER FROM THE PULP, PAPER, AND PAPERBOARD INDUSTRY

Priority pollutants

benzene
chlorobenzene
1,2-dichloroethane
1,1,1-trichloroethane
1,1-dichloroethane
1,1,2,2-tetrachloroethane
trichlorophenol*
chloroform
2,4-dichlorophenol
ethylbenzene
fluoranthene
methylene chloride
dichlorobromomethane
trichlorofluoromethane
chlorodibromomethane
isophorone
naphthalene
phenol
bis(2-ethylhexyl) phthalate
di-n-butyl phthalate
di-n-octyl phthalate
diethyl phthalate
chrysene
anthracene/phenanthrene
tetrachloroethylene
toluene
trichloroethylene

Nonconventional pollutants

oleic acid
linoleic acid
lonolenic acid
pimaric acid
isopimaric acid
dehydroabietic acid
abietic acid
3,4,5-trichloroguaiacol
tetrachloroguaiacol
monochlorodehydroabietic acid
dichlorodehydroabietic acid
9,10-epoxystearic acid
9,10-dichlorostearic acid
xylenes

*Includes 2,4,5- and 2,4,6-trichlorophenol

SOURCE: EPA 440/1-82-025 (1982)

mixed. The long residence times make these systems relatively insensitive to shock loading. Design specifications assume approximately 1.25 mg oxygen supplied/mg BOD removed using mechanical aerators which supply 1.06 kg oxygen/kW-hr.

Conventional activated sludge systems can also be used for bio-oxidation with approximately 6-8 hour residence times in well mixed systems. These systems are more susceptible to upsets due to shocks and require secondary clarifiers for removal and return of sludge. Design specifications used on the effluent guidelines study included an oxygen requirement of 1.0 mg oxygen/mg BOD removed supplied by aerators with a transfer efficiency of 0.34 Kg oxygen/Kw-hr. High rate trickling filters have been used upstream of aerated stabilization systems to reduce high organic loadings (Gehm, et al. 1965).

MODEL TREATMENT PLANTS

Hazardous waste generators and management facilities have been reported to be concentrated in the manufacturing industries. (Westat, 1984). Eighty five percent of the 14,098 generators and 72 percent of the 4,818 TSD facilities are estimated to be associated with industrial manufacturing codes 2000 through 3999. (See Table 5).

The wastes from these generators include solvent, corrosives, sludges, etc. They are subject to various forms of handling prior to and during disposal. Those processes involving the use of air (biological treatment and cooling), or subject to the introduction of air (stirred equalization and neutralization) are subject to emit VOC as a consequence of air stripping.

In general, these processes can be categorized as biological or physical-chemical, depending on the unit process involved. For the purposes of this report, this distinction will be maintained. Further, only those biological processes or physical-chemical processes with potential to vent to the air will be addressed. Anaerobic processes, including anaerobic sludge digestion have been excluded because the enclosed nature of these systems substantially reduces air emissions.

Aerobic biological treatment is only economically viable for the destruction of organics when the waste stream is large, continuous, fairly consistent in composition and of low toxicity. Consequently, biological systems are viable for a limited range of treatment, primarily for dilute streams with low

TABLE 5. GENERATORS AND TSD BY INDUSTRY TYPE
(Westat, 1984)

Description	Generators	TSD*
Fabricated metal products	2,636	1,249
Chemicals	2,443	547
Electrical equipment	1,515	540
Other metal related products	2,222	804
Nonmanufacturing	2,074	800

*Treatment, storage, and disposal facilities.

metal concentrations in order to reduce the potential of biostatic and/or biotoxic side effects. As such, biological treatment would not be a principal factor in the treatment of hazardous wastes at generator or TSDF sites. Rather they would serve to clean up other aqueous streams which have been contaminated or which have been combined with low levels of toxicants.

Normally, physical, chemical, or some combination of physical-chemical treatment process will be used for actual hazardous waste treatment at generator or TSD sites. These processes may include air stripping, equalization, cooling, neutralization, evaporation, all of which have potential for air emissions.

Biological treatment is generally a subset of an overall treatment system that may also include physical and chemical processes. A typical arrangement of units will include preliminary treatment processes, primary treatment, secondary treatment with sedimentation, optional tertiary treatment, sludge handling, and ultimate disposal.

The design and function of these units have been thoroughly discussed in the literature. In general, they perform the following functions. Preliminary treatment involves the screening and degritting of raw wastewater. In this step coarse materials are collected on bar screens (1.3 to 5.1 cm spacing) for burial, and heavier inorganic particulates are removed through selective deposition in velocity control chambers.

Primary treatment involves detention of wastewater in either rectangular or circular basins for 1-2 hours in order to allow readily settleable organic solids to be removed via gravity induced sedimentation. Primary treatment can also involve the introduction of microscopic air bubbles into the wastewater as occurs with a dissolved air flotation unit (DAF) in order to float oils and grease to the surface where they are removed by skimmers for disposal.

Secondary treatment can include some physical and chemical processes, but typically this is the domain of biological treatment processes. These processes include trickling filters and modifications of the activated sludge process. These processes will be further discussed under each model plant heading.

Tertiary treatment involves the removal of those pollutants not removed by the conventional biological processes contained in secondary treatment. These pollutants include suspended solids, BOD (typically less than 10-15 mg/l), refractory organics, nutrients, and inorganic salts. The tertiary treatment option selection largely depends on the water quality requirement.

Sludge handling involves the stabilization of the solid-water mixtures derived from the primary and secondary clarifier as well as the excess biomass from the activated sludge process and chemical reactions. These mixtures undergo thickening, anaerobic or aerobic digestion and dewatering prior to ultimate disposal. Anaerobic digestion is designed for minimal air/sludge contact. Emissions from the other processes are likely to be insignificant because the upstream processing units will have provided extensive opportunities for volatilization prior to the sludge handling operations.

Because the focus of this work involves the identification and modeling of the competing mechanisms of pollutant removal, five general model systems have been described that center on the use of air and aeration process. These models are:

1. Trickling filtration
2. Activated sludge (mechanical aeration)
3. Activated sludge (diffused aeration)
4. Activated sludge - aerated lagoons (mechanical aeration)
5. Spray Ponds - (mechanical spray)

Although presented as discrete model systems, it should be noted that portions of these model plants are interchanged with other model plants, and that all model plants can be composed of unit processes that fit into the broad categories of treatment previously described. A good example of the former situation is the use of a trickling filtration unit in the treatment train ahead of an activated sludge unit. In this capacity, the trickling filter operates as a roughing filter to pretreat industrial wastes prior to secondary treatment and not as a secondary treatment process.

It should be emphasized that treatment systems vary widely depending on the nature of the wastewater, the availability of land, prior regulatory pressure, the composition and flow rate that may have existed at the time the system was designed, and many other factors. The model systems that follow d not represent an "average" system. These systems do fall within the range of sizes and configurations that may be encountered at TSDFs.

Model Plant #1. Trickling filtration

The typical trickling filter plant consists of the following units: pretreatment, primary clarifier, trickling filter, secondary clarifier and post-treatment unit (see Figure 1). The heart of the system is the trickling filter itself, which consists of a circular basin 1-2.4 m deep packed with a bed of either rock or plastic media, over which wastewater is sprayed. A zoogleal slime which attaches to the media assimilates and oxidizes the organics in the wastewater. Oxygen and organic matter diffuse into the zoogleal mass and end products of oxidation counter-diffuse back into the flowing liquid or to the void spaces. The treated water and any particulates from the filter bed are collected in an underdrain system and sent to secondary clarifiers for sedimentation.

The packing media is typically dosed with a rotary distributor which sprays the waste over the media. The media may be either plastic or rock. The rock medium represents a traditional approach; the plastic however, offers advantages such as lower specific weights and higher void spaces and is amenable to above ground installation.

The performance of the unit is affected by many factors such as hydraulic and organic loadings, depth and physical characteristic of the media, the method of wastewater distribution, ventilation, and characteristics of the applied wastewater (Eckenfelder, 1970). Municipal wastewater and a wide variety of industrial wastewaters are amenable to treatment in trickling filters.

The principal components of the trickling filter process are:

1. The distribution system
2. The filter media
3. The underdrain
4. Final sedimentation

The rotary distributor consists of two or more horizontal arms mounted on a turntable assembly anchored to a center column. The wastewater is uniformly distributed over the media through orifices located in the arms. The principal drive mechanism for these arms is the reaction force from the spray on the radial arms. The arms are sized to limit velocities to 1.2 m/sec at maximum flow. The rotation speed of the arms varies with flow rate in the range of 0.1-2 rpm.

Ventilation is extremely important in achieving efficient filter operation. Usually, if the underdrain is properly sized, the differences in air and water temperature will provide a natural driving force for ventilation. An air flow

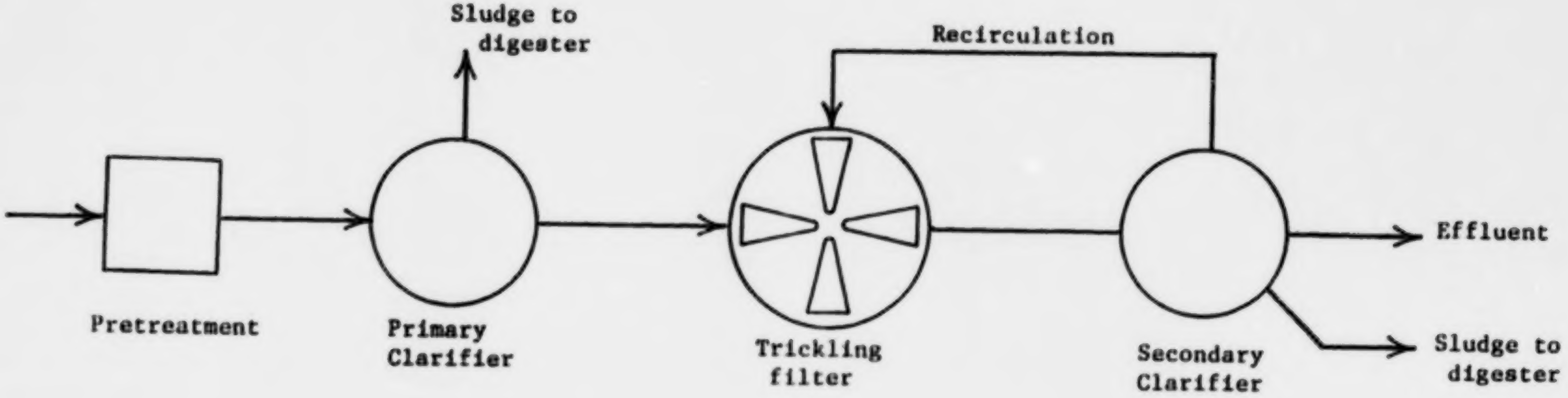

Sludge to digester
Recirculation
Pretreatment
Primary Clarifier
Trickling filter
Secondary Clarifier
Effluent
Sludge to digester

Figure 1. Model trickling filter plant.

rate of approximately 0.03 m^3/m^2 filter area per minute is required to sustain aerobic conditions within the bed. When forced ventilation systems are required, they are typically designed to provide an air flow of 0.3 m^3/m^2 of filter area per minute.

Organic and hydraulic loading determines the classification of the filters: low-rate, high-rate, or roughing-rate. Low-rate filters are generally not equipped with recirculation and are rarely used. High-rate filters use recirculation to dilute the influent organic strength and to flush the media voids. This permits higher BOD loadings per volume of media and promotes the return of activated organisms as a seed. The high-rate filters are generally designed to accept a continuous flow of wastewater and may be either single stage or two staged. High-rate filters also have a number of modifications of the basic recirculation scheme.

Roughing rate trickling filters provide an intermediate stage of treatment and are used frequently to precede activated sludge units or second stage filters. The purpose of this operation is to reduce high organic loadings prior to further treatment. This intermediate stage is typical for industrial systems.

The trickling filter model is based on a design (EPA-430/9-77-006) currently in operation in a U.S. municipality (See Figure 1). It represents a single train of a multi-train high rate process. The operating conditions and specifications fall within the range expected for industrial waste treatment.

The design parameters are given in Table 6.

Conventional Activated Sludge System

The typical configuration of an activated sludge system is pretreatment, optional primary sedimentation followed by the aeration process including secondary clarification, and post treatment (e.g., Figure 2). The principal treatment process is the aeration tank. This is a continuous flow, biological treatment process characterized by the turbulent suspension of microscopic aerobes. The turbulence promotes mixing and induces a relatively homogenous state in which the microbes are able to absorb and oxidize soluble and colloidal organics. The process involves an aeration step followed by a solid-liquid separation step in which part of the separated sludge is recycled back to the system for mixing with the raw influent.

TABLE 6. MODEL PLANT OPERATIONAL PARAMETERS - TRICKLING FILTER

Plant Flow:	6.4 MGD (0.28 m^3/sec)	Plant Performance:	85% BOD Removal 75% Suspended Solids Removal
Influent BOD-183 mg/l			
Influent Suspended Solids - 188 mg/l			
Trickling Filter:	Diameter	190 ft	(58 m)
	Depth	5 ft	(1.5 m)
	Area	28353	(2640 m^2)
	Volume	141764 ft^3	(3960 m^3)
	Hydraulic loading	29 MGD/acre	(1.1 m^3/m^2-hr)
	Recirculation -	190%	
Clarifiers:	Diameter	100 ft	(30 m)
	Depth	9.2 ft	(2.8 m)
	Area	7854 ft^2	(730 m^2)
	Weir height	1 ft	(30 cm)
	Surface loading -	1350 gal/ft^2/day	(0.47 m^3/m^2-day)
	Detention time -	1.2 hours	

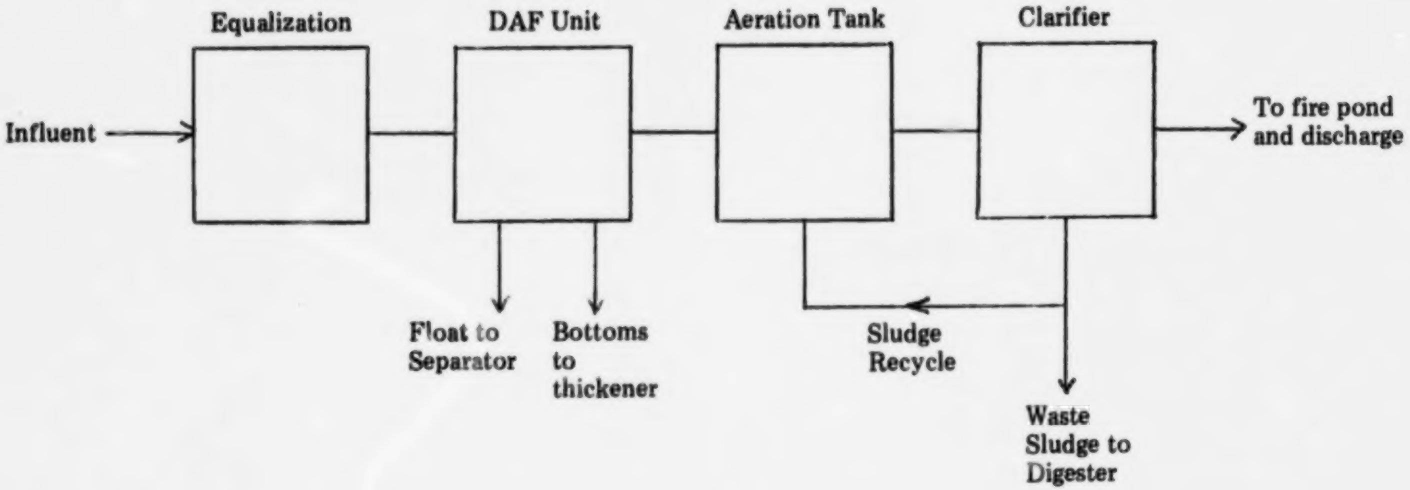

Equalization
DAF Unit
Aeration Tank
Clarifier
Influent
To fire pond and discharge
Float to Separator
Bottoms to thickener
Sludge Recycle
Waste Sludge to Digester

Figure 2. Conventional activated sludge system with mechanical aeration.

There are many variations of the activated sludge process; however, they generally can be reduced to looking at either the loading rates in terms of BOD or the physical arrangement of the process train. The loading is typically one of three basic types. High rate takes advantage of the settleability of sludge when the system is loaded at a rate of 0.80-1.15 g of BOD/g of mixed liquor suspended solids per day. Conventional rate is of the range 0.2 to 0.5 g BOD/g mixed liquor volatile suspended solids per day. This rate is typical for most larger municipal treatment plants. Extended aeration rate is the lowest range of process loading and is used in those plants which are small in size and do not receive 24 hour supervision. As such they are generally conservatively designed and operate in the range of 0.05-0.15 g of BOD applied/g of MLVSS/day. Industrial wastewaters vary widely in terms of influent concentration and biodegradability. Thus, a wide range of loading rates are used depending on individual circumstances.

Physical arrangements are of three types; the complete mix activated sludge, plug flow activated sludge, and activated sludge with reaeration. In the complete mix arrangement, the return sludge and the wastewater are uniformly introduced into the aeration basin through several points in order to obtain a homogeneous mixture. In a plug flow arrangement both the untreated wastewater and the return sludge are introduced at the head of the plant and flow through the plant in a modified plug flow. Such plants are often compartmentalized to maintain the plug flow regime. Activated sludge with sludge reaeration constitutes a rearrangement of process streams. In this instance the sludge is compartmentalized and aerated prior to its contact with the untreated waste.

Model Plant #2 Conventional Activated Sludge (Mechanical Aeration)

The principal component of the mechanical aeration system is the aerator. There are two types in general use today, surface aerators and turbine aerators. The surface aerator is highly developed and widely used, particularly in the treatment of industrial waste. The surface aerators may either float or be mounted on supports in the aeration basin. They enhance the entrainment of atmospheric air in the aeration basin by producing a region of high turbulence around the periphery of the aerator. Oxygen transfer efficiency of these aerators increases with the depth of submersion, as does power cost; consequently, there is a trade off between efficiency and cost.

Since 1950, the submerged turbine has been widely used in the chemical industry. It offers an attractive means of upgrading existing facilities to handle increased loads. These aerators are used because of improved oxygen transfer efficiency and lower horsepower requirements. Oxygen transfer efficiency for aerators, as rated in terms of mass of oxygen transferred per energy input, is typically on the order of 1.2 Kg O_2/KW-hr (2 lb O_2/hp-hr). Air and energy requirements for an aeration system are typically on the order of 50-90 m^3/Kg BOD removed and 0.040 to 0.26 Kw/m^3 of basin volume. The mechanical aeration model shown in Figure 2 is based on a portion of a plant currently operating at an oil refinery (U.S. EPA, EMB Report 85-HWS-3) (see Table 7).

The mechanical aerator approach is found in large open basins particularly in those plants operating in a complete mix, conventional activated sludge mode. The turbulence introduced by the rotary action of the aerator blades promotes a homogeneous mixing and enhances the overall complete mix mode of operation.

Model Plant #3: Conventional Activated Sludge (Diffused Air: Coarse and Fine Bubble)

A second approach to aeration is the use of diffuser systems which are generally used in plug flow systems and sludge reaeration systems, the most common types of aeration systems used in activated sludge plant. The distribution system consists of an array of diffusers situated near the bottom of the basin. These diffusers are designed to produce either coarse or fine bubbles and are supplied with air by compressors. In the period from 1950-1978, the fine bubble systems were in wide use. At that time, it was felt that the increase in oxygen transfer efficiency of the smaller bubble diameter (8% vs. 5% for the coarse bubble) was important. Later, however, inefficiencies such as clogging decreased the overall attractiveness of these systems.

The most common type of fine bubble diffusers are nylon or dacron socks and saran wrapped tubes. Other systems include porous ceramic plates that generate small diameter bubbles. Coarse bubble diffusers can be tubes covered with synthetic fabric or wound with filaments, and sprayers with multiple openings created by drilling holes in pipes or loosely attaching plates or discs to a supporting piece of pipe. Although the oxygen transfer efficiency is lower, coarse bubble diffusers do not suffer from clogging and have lower

TABLE 7. MODEL PLANT #2 CONVENTIONAL ACTIVATED SLUDGE WITH MECHANICAL AERATION. OPERATIONAL PARAMETERS

Plant Flow: 1.5 MGD (0.066 m^3/sec) Plant Performance 85% BOD Removal

Plant Loading: Influent BOD - 80 mg/l

Aeration Basin (Mechanical Aeration)

aerators	- 2, 75 Hp each	(56 Kw each)
length	- 141 ft	(43 m)
depth	- 12 ft	(3.7 m)
width	- 69 ft	(21 m)
area	- 9715 ft^2	(910 m^2)
Detention time - 14 hours at average flow		

Clarifier

Length	75 ft	(23 m)
Depth	9.8 ft	(3.0 m)
Area	740 ft^2	(40 m^2)
Weir height	1 ft	(30 cm)
Surface loading	2030 gal/ft^2/day	(140 m^3/m^2-day)
Detention time	0.5 hours	

initial cost and maintenance. Many treatment plants are reported to have switched to the coarse bubble systems in order to take advantage of these features.

The model plant for this system based on typical organic chemical manufacturing wastewater (EPA-450/3-80-025) is described in Figure 3 and Table 8.

Model Plant #4: Aerated Lagoons (Mechanical Air)

Aerated lagoon systems are medium depth basins designed for biological treatment on a continuous flow basis. They are equipped with surface aerators and are primarily used to treat wastes of low-medium strength in areas where land is inexpensive. They are not as widely used as stabilization ponds, but their feasibility has been fully demonstrated and they may represent an upgrading of an oxidation pond.

Aerated lagoons have detention times on the order of 3-10 days. Aerated lagoons are staged in series and are designed to achieve partial mixing. Consequently, aerobic and anaerobic stratification can occur. A large fraction of the incoming solids may in fact settle out near the head of the plant.

The model proposed for this type of treatment system (See Figure 4) is based on a system at an existing manufacturing facility (Alsop, et al. 1984) (see Table 9).

Model Plant #5: Spray Evaporation Ponds

Spray evaporation ponds are used primarily to reduce the amount of water contained in a waste. Biodegradation in these ponds may be relatively unimportant. These are basically ponds equipped with submersible pumps attached to vertical pipes ending in standard irrigation spray headers. Water is pumped through this system and dispersed in the air. As the droplets fall back to the pond they are enriched with oxygen and subjected to evaporative processes. These ponds occur primarily in waste treatment systems involving large quantities of recycled water. Operational parameters are given in Table 10. Evaporation ponds without spray headers are termed solar evaporation ponds and are not intentionally aerated.

Physical-Chemical Treatment System

Physical-chemical processes are generally defined as those operations which effect the removal and/or destruction of undesirable constituents in wastewater by means other than biological degradation or biological conversion.

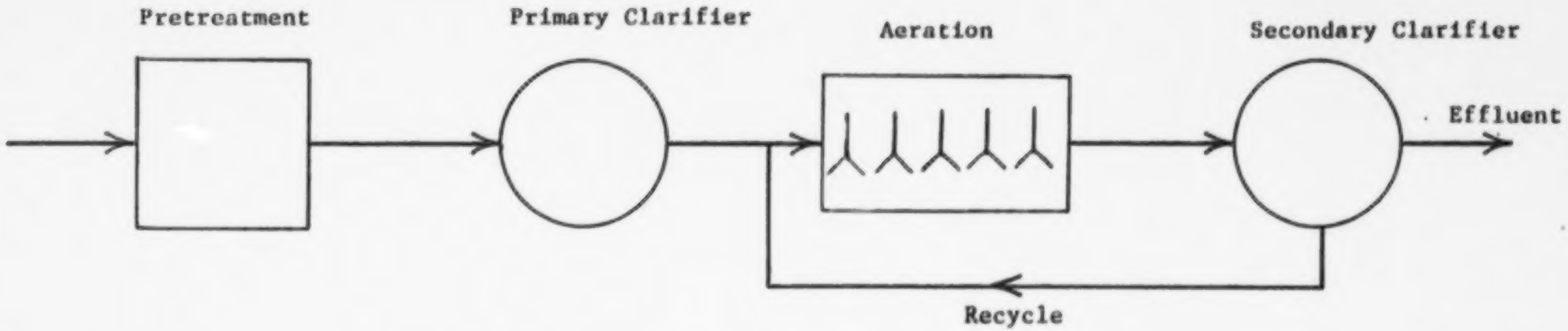

Pretreatment
Primary Clarifier
Aeration
Secondary Clarifier
Effluent
Recycle

Figure 3. Conventional activated sludge with diffused aeration model plant.

TABLE 8. MODEL PLANT #3 CONVENTIONAL ACTIVATED SLUDGE WITH DIFFUSED AERATION. OPERATIONAL PARAMTERS

Plant flow 4.5 MGD (0.2 m^3/sec) Plant Performance 85% BOD Removal

Plant loading:		
Influent BOD	2000 mg/L	
Aeration Basin (Sparger)		
Av scfm	21,600	(612 m^3/min)
length	260 ft	(79 m)
depth	20 ft	(6 m)
area	68,000 ft^2	(6,300 m^2)
Detention time	2 days @ average flow in aeration basin	
Clarifier		
Diameter	49 ft	(15 m)
Depth	9.8 ft	(3 m)
Area	1,900 ft^2	(180 m^2)
Weir height	1 ft	(30 cm)
Detention time	3.0 hours	

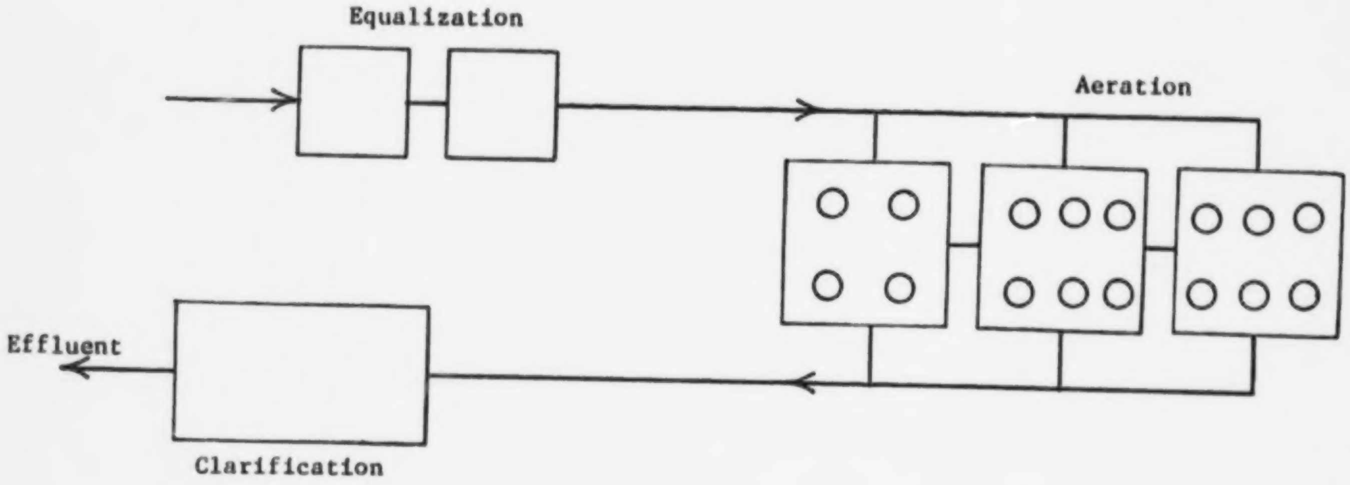

Equalization
Aeration
Effluent
Clarification

Figure 4. Aerated lagoon model plant.

TABLE 9. MODEL PLANT #4 AERATED LAGOON. OPERATIONAL PARAMETERS

Plant Flow 5.3 MGD (0.23 m^3/sec) Plant performance: 80% BOD Removal
Plant Loading: Influent BOD = 2000 mg/L

Aeration Basins

2 basins		
aerators	10 @ 100 hp each, 5 @ 75 hp each	
length	560 ft	(170 m)
depth	12 ft	(3.6 m)
width	280 ft	(85 m)
Area	157,000 ft^2	

Detention time - 250 hours

Clarifiers (2)

Depth	10 ft	(3 m)
Area	5675 ft^2	(527 m^2)
Diameter	85 ft	(26 m)
Weir height	1 ft	(30 cm)

Surface loading - 148 gal/ft^2/day (6.1 m^3/m^2-day)
Detention time - 13 hours

Preliminary Holding (Equalization)

Depth	14 ft	(4.3 m)
Length	310 ft	(94 m)
Width	180 ft	(55 m)
Area	56,000 ft^2	
Detention time -	51 hours	

TABLE 10. MODEL PLANT #5 SPRAY EVAPORATION POND. OPERATIONAL PARAMETERS

Pond capacity: 1 MGD (0.043 m^3/sec)

Pond loading:
Influent BOD 100 mg/l
Influent suspended solids N/A

Pond

Depth	10 ft	(3.0 m)
Length	134 ft	(41 m)
Width	100 ft	(30 m)
Area	13369 ft^2	(1240 m^2)

Nozzle capacity 40 gal/min (2.5 L/sec)
6 feet above pond surface
(1.8 m above pond surface)

Physical-chemical processes include a wide array of traditional and innovative processes. For the purpose of this report, however, the focus is placed on those processes which are intentionally aerated. These processes include dissolved air flotation, and mechanically agitated equalization/neutralization basins. These processes can be used as adjuncts to the model plant flow charts presented in this section.

Dissolved Air Flotation (DAF)

Dissolved air flotation is widely used in industry to remove suspended solids by flotation. The flotation of the particulate is induced by microscopic air bubbles attaching to the particulate or agglomerate and giving it buoyancy. Particles are floated to the surface where they are removed by skimmers for further treatment.

The DAF system generates a supersaturated solution of wastewater and air by pressurizing either the influent wastewater (or a side stream of the influent wastewater) and introducing compressed air. The pressure is then released in the detention tank generating the numerous microscopic bubbles which adhere to particulates or are trapped by any floc which may be present. The design criteria for a model DAF unit are contained in Table 11.

Neutralization (Equalization) Process

Although neutralization and equalization units perform different functions, i.e., pH neutralization vs. flow equalization, these operations can be considered together as they permit similar modes of air/water contact. Primarily, these units are open basins or tanks with varying size depending upon the desired retention time. Mechanical agitation by stirrers is used to assure a homogeneous mixture. The design criteria for these processes are dependent on the variation in influent composition. For example, when the objective is equalization, more erratic fluctuations in the influent composition necessitates longer residence times.

TABLE 11. OPERATIONAL PARAMETERS - DISSOLVED AIR FLOTATION

Flow	-	5 MGD	(0.22 m^3/sec)
Pressure	-	25-70 psig	(1.7 - 4.8 atm gauge)
Detention time	-	0.25 - 1 hr	
Surface loading	-	500-8000 gpd/ft^2	(0.17 - 2.8 m^3/m^2-day)
Recycle	-	5-120%	
Solids loading	-	.5-5 lb/ft^2/hr	(2.4 - 24 kg/m^3 hr)
Air to solids ratio	-	.01 - .1 lb/lb	(.01 - 0.10 kg/kg)
Depth	-	4-9 feet	(1-3 m)

SECTION 4

DESCRIPTION OF REMOVAL MECHANISMS

BACKGROUND

VOCs are removed from wastewater through destructive and nondestructive mechanisms. The major destructive mechanism is biological oxidation. Of less importance are chemical reactions, which also destroy specific VOCs through conversion to other materials. The major nondestructive removal mechanism is mass transfer from the liquid phase to the atmosphere. This takes place in a variety of processes that offer the opportunity for air/water contact. A less important nondestructive removal mechanism results from preferential adsorption of VOCs on surfaces (chiefly biomass solids). The effect of adsorption on solids can be determined through accurate measurements and analyses of net solids removal from process units.

A generalized mass balance applicable to either individual processes or complete treatment systems is given in Equation 1.

$$\text{(Mass In)} - \text{(Mass Out)} = \text{(Mass Destroyed)} + \text{(Mass transferred to air)} + \text{(Mass transferred to solids)} \qquad (1)$$

The following sections deal with biological oxidation, mass transfer, and adsorption.

BIOLOGICAL OXIDATION

Biological wastewater treatment processes involve contacting contaminated wastewater with microorganisms capable of using the organic contaminants present in the wastewater as food. Aerobic processes have been used most often for wastewater treatment. In these processes, which include activated sludge, trickling filters, aerated lagoons and spray ponds, microorganisms present in the wastewater (or supported on media in the case of trickling filters) use oxygen dissolved in the wastewater to convert the contaminants to more oxidized forms and to produce more organisms. The ultimate oxidation products of organics are carbon dioxide and water and when reactions go to completion, they proceed in accordance with the chemical equations for complete combustion of hydrocarbons. Intermediate products include biomass and partially oxidized hydrocarbons.

The rates of reaction for biological oxidation are dependent upon many factors including the presence or absence of nutrients, the presence or absence of inhibitors, the other oxidizable compounds present in the wastewater, the temperature, and the concentration of biomass in the system. Various investigators have attempted to determine the biodegradability of specific organic components under aerobic conditions. No standard procedure has been adopted for experiments of this kind and extrapolations of laboratory and pilot scale data to real systems, either for design calculations or emissions estimation must be made with caution.

Classical Approach

The conceptual approach to biooxidation which is used most commonly by sanitary engineers follows the model of Lawrence and McCarty (1970). The production of biomass is related to the utilization (and thus disappearance) of the organic material as

$$\frac{dX_B}{dt} = Y_B \frac{dC_p}{dt} - k_d X_B \tag{2}$$

where

X_B = concentration of biomass, mg/L which is typically estimated by determination of volatile suspended solids content

t = time, days

Y_B = growth yield, i.e., the mass of biomass produced per mass or organic material consumed

C_p = concentration of organic pollutant, mg/L

k_d = first order biomass decay coefficient (i.e., the biomass die off rate), day^{-1}.

The model of Lawrence and McCarty (1970) then describes the biooxidation process in terms of two additional constants,

$$\frac{1}{X_B} \frac{dC_p}{dt} = \frac{k_{max} C_p}{k_{half} + C_p} \tag{3}$$

where

k_{max} = the maximum rate at which organic pollutant can be consumed by biomass, $(\text{mg/L day})_{\text{pollutant}}/(\text{mg/L})_{\text{biomass}} = \text{day}^{-1}$

k_{half} = pollutant concentration at which the rate of pollutant consumption per mass of biomass is one-half of the maximum rate, mg/L.

Equation (2) describes a kinetic rate expression in which the order of rate dependency is variable depending on the concentration of the pollutant. While this is inconvenient, it has been found to accurately explain the biodegradation of organic material in a wide variety of systems and is generally accepted. The four constants describing the system; Y_B, k_d, k_{max}, and K_{half} are available for a very limited number of pure compounds and mixed industrial wastes. A laboratory procedure for obtaining these constants is given by Metcalf and Eddy (1972). Kincannon and Stover (1983) have reported experimental values for certain chemical and plastic manufacturing wastewaters.

Rates from the EPA Data Base

While the literature data on biodegradability were not obtained under standardized procedures, some qualitative judgments regarding individual compounds can be made. Where several components were tested using the same procedure, the observed rates of biodegradation can be ranked in relative order. The most extensive compilation available is that of Pitter (1976) which includes biodegradation data for 123 organic compounds (see Table 12). Pitter's work involved pure solutions of chemicals formulated to represent 200 mg/L of chemical oxygen demand. Carefully acclimated inocula were used. Blackburn et al. (1982) conducted an extensive literature review of biodegradability and biodegradation rate studies. A list of biodegradation rates converted to a basis roughly comparable to that of Pitter is given in Table 13. Specific compound removal rates have also been converted to theoretical oxygen demand (ThOD) removal rates in this table. In practice, these rates are applicable to suspended growth reactors such as activated sludge and aerated lagoon processes. The relative rates may be applicable to trickling filter processes.

One of the difficulties in interpreting biodegradation data obtained by different investigators is the limitation on rates imposed by the influent substrate concentration. Where the compound in question is completely degraded over the course of the test, a minimum rate is obtained because had more of the compound been present, a greater amount might have been oxidized in the same period of time. Similarly, although biooxidation of organic chemicals is

TABLE 12. BIODEGRADATION DATA FROM PITTER (1976)

Compound	Rate of biodegradation (mg COD g^{-1} h^{-1})	Compound	Rate of biodegradation (mg COD g^{-1} h^{-1})
Ammonium oxalate	9.3	2,3-Dimethylphenol	35.0
n-butanol	84.0	2,4-Dimethylphenol	28.2
Sec. butanol	55.0	3,4-Dimethylphenol	13.4
Tert. butanol	30.0	3,5-Dimethylphenol	11.1
1,4-Butanediol	40.0	2,5-Dimethylphenol	10.6
Diethylene glycol	13.7	2,6-Dimethylphenol	9.0
Diethanolamine	19.5	3,4-Dimethylaniline	30.0
Ethylene diamine	9.8	2,3-Dimethylaniline	12.7
Ethylene glycol	41.7	2,5-Dimethylaniline	3.6
Glycerol	85.0	2,4-Diaminophenol	12.0
Glucose	180.0	2,5-Dinitrophenol	0
n-Propanol	71.0	2,6-Dinitrophenol	≅0
Iso-Propanol	52.0	2,4-Dinitrophenol	6.0
Triethylene glycol	27.5	3,5-Dinitrobenzoic acid	-
Borneol	8.9	3,5-Dinitrosalicylic acid	-
Caprolactam	16.0	Furfuryl alcohol	41.0
Cyclohexanol	28.0	Furfurylaldehyde	37.0
Cyclopentanol	55.0	Gallic acid	20.0
Cyclohexanone	30.0	Gentisic acid	80.0
Cyclopentanone	57.0	p-Hydroxybenzoic acid	100.0
Cyclohexanolone	51.5	Hydroquinone	54.2
1,2-Cyclohexanediol	66.0	Isophthalic acid	76.0
Dimethylcyclohexanol	21.6	Metol	0.8
4-Methylcyclohexanol	40.0	Naphtoic acid	15.5
4-Methylcyclohexanone	62.5	1-Naphthol	38.4
Menthol	17.7	1-Naphthylamine	0
Tetrahydrofurfuryl alcohol	40.0	1-Naphthalenesulfonic acid	18.0
Tetrahydrophthalimide	0	1-Naphthol-2-sulphonic acid	18.0
Tetrahydrophthalic acid	0	1-Naphthylamine-6-sulphonic acid	0
Aniline	19.0	2-Naphthol	39.2
Aminophenolsulphonic acid	7.1	p-Nitroacetophenone	5.2
Acetanilide	14.7	Nitrobenzene	14.0
p-Aminoacetanilide	11.3	o-Nitrophenol	14.0
o-Aminotoluene	15.1	m-Nitrophenol	17.5
m-Aminotoluene	30.0	p-Nitrophenol	17.5
p-Aminotoluene	20.0	o-Nitroluene	32.5
o-Aminobenzoic acid	27.1	m-Nitrotoluene	21.0
m-Aminobenzoic acid	7.0	p-Nitrotoluene	32.5
p-Aminobenzoic acid	12.5	o-Nitrobenzaldehyde	13.8
o-Aminophenol	21.1	m-Nitrobenzaldehyde	10.0
m-Aminophenol	10.6	p-Nitrobenzaldehyde	13.8
p-Aminophenol	16.7	o-Nitrobenzoic acid	20.0
Benzenesulphonic acid	10.6	m-Nitrobenzoic acid	7.0
m-Benzenedisulphonic acid	3.4	p-Nitrobenzoic acid	19.7
Benzaldehyde	119.0	o-Nitroaniline	0
Benzoic acid	88.5	m-Nitroaniline	0
o-Cresol	54.0	p-Nitroaniline	0
m-Cresol	55.0	Phthalimide	20.8
p-Cresol	55.0	Phthalic acid	78.4
D-Chloramphenicol	3.3	Phenol	80.0
o-Chlorophenol	25.0	Phloroglucinol	22.1
p-Chlorophenol	11.0	Pyrocatechol	55.5
o-Chloroaniline	16.7	Resorcinol	57.5
m-Chloroaniline	6.2	Salicyclic acid	95.0
p-Chloroaniline	5.7	Sulphosalicyclic acid	11.3
2-Chloro-4-nitrophenol	5.3	Sulphanilic acid	4.0
2,4-Dichlorophenol	10.5	Thymol	15.6
1,3-Dinitrobenzene	-	p-Toluenesulphonic acid	8.4
1,4-Dinitrobenzene	-	2,4,6-Trinitrophenol	0

typically regarded as a reaction which proceeds with a zero order dependence on the concentration of the organic material, at very low organic concentrations this may not be true.

The biooxidation rates listed in Table 13 should be considered as minimums for well designed well operated systems. Better acclimated full-scale systems might perform more efficiently under some circumstances. More importantly, poorly designed, poorly operated systems can be expected to have much lower, or in some cases zero, rates of biooxidation. The presence of toxic or inhibiting materials in the wastewater or lack of nutrients can adversely affect removal rates. Shock loadings of material which may be rapidly biodegradable under normal conditions can cause process upsets which greatly reduce treatment plant efficiency. In addition, low temperatures will depress the biooxidation rate and cause seasonal fluctuations in plant performance.

The best estimates of treatment efficiency to be expected under real conditions will be based on mass balance data from existing plants treating similar wastes. Air emissions data are rarely available, however, and the actual destruction efficiency of the treatment plant generally must be estimated by calculating expected air emissions based on effluent concentration data. Where specific organic compounds are present in the effluent in concentrations below the detection limit, this calculation is not possible.

The application of laboratory and field data to emissions estimation is imprecise because the laboratory data are obtained under conditions which may not accurately reflect the varying and uncontrolled nature of full-scale systems. Data obtained from larger scale systems may be inaccurate due to difficulty in sampling. Deviations from ideal flow (e.g., completely mixed stirred tank) may result in errors due to nonrepresentative sampling. Real systems may have influent flow rates which vary; calculation of residence times associated with particular effluent samples may be subject to uncertainty.

Notwithstanding the uncertainties inherent in the bioxidation data abstracted from the literature, these data are the best alternative for use in predictive emissions models if no full-scale system using similar waste in a similar flow scheme is available. Where no data are available for a particular compound, the approach of Strier (1982, 1985) can be used to obtain an estimate of the relative importance of biological oxidation, air stripping, and adsorption on sludge in a wastewater treatment plant. A description of this approach is given in the section titled Predictive Fate Models.

TABLE 13. BIOOXIDATION RATES FROM EPA DATA BASE

Compound	Initial concentration mg/L	Biomass concentration mg/L	Biodegradation Rate		Reference
			mg compound/g hr	mg ThOD/g hr	
Ethyl acetate	167	1,000[a]	21	53[b]	Stover and Kincannon, 1981
1,2-Dichloroethane	258	1,000[a]	32	51[b]	Stover and Kincannon, 1981
Phenol	173	1,000[a]	22	57[b]	Stover and Kincannon, 1981
	250	2,000	26	6.2	Stamoudis et al., 1979
	400	2,244	6.8	16	Radakrishnon et al., 1974
	1,000	2,000	21	50	Capestany et al., 1977
1,2-Dichlorobenzene	83	1,000[a]	10	46[b]	Stover and Kincannon, 1981
Benzene	153	1,000[a]	19	52[b]	Stover and Kincannon, 1981
Nitrilotriacetate	500	3,500	43	37	Swisher et al., 1967
	110	1,760	5.2	4.5	Pfeil and Lee, 1968
Cresols	233	2,000	2.4	6.0	Stamoudis et al., 1979
Tetrachloroethane	201	1,000[a]	24	59[b]	Stover and Kincannon, 1981
Nitrobenzene	100	1,000[a]	12	80[b]	Stover and Kincannon, 1981
Dichlorophenol	75	1,000[a]	8.9	64[b]	Stover and Kincannon, 1981
Acrolein	62	1,000[a]	7.8	46[b]	Stover and Kincannon, 1981
Acrylonitrile	152	1,000[a]	19	51[b]	Stover and Kincannon, 1981
1,2-Dichloropropane	182	1,000[a]	23	55[b]	Stover and Kincannon, 1981
Methylene chloride	180	1,000[a]	22	55[b]	Stover and Kincannon, 1981
Methanol	500	3,270	1.0	1.5	Placek et al., 1947
	500	1,000	12	18	McKinney et al., 1955
Ethanol	1,000	1,740	5.9	12	Placek et al., 1947
	500	1,000	11	23	McKinney et al., 1955

TABLE 13 (continued)

Compound	Initial concentration mg/L	Biomass concentration mg/L	Biodegradation Rate mg compound/g hr	Biodegradation Rate mg ThOD/g hr	Reference
Formaldehyde	720	2,600	0	0	Placek et al., 1947
Acetic acid	600	2,500	4.0	43	Placek et al., 1947
	200	350	>1.5	>1.6	Englebrecht et al., 1957
	1,500	1,440	88	94	Sato et al., 1972
Oxalic acid	2,000	3,500	36	4.6	Nelson et al., 1954
Trinitrotoluene	25	1,180	28	3.8	Nay et al., 1974
n-Propanol	500	1,000	12	29	McKinney et al., 1955
i-Propanol	500	1,000	11	26	McKinney et al., 1955
n-Butanol	500	1,000	10	26	McKinney et al., 1955
i-Butanol	500	1,000	10	26	McKinney et al., 1955
2-Butanol	500	1,000	12	31	McKinney et al., 1955
t-Butanol	500	170	2.6	6.7	McKinney et al., 1955
Aminobenzoic acid	20	30	220	475	Gerike et al., 1980
Chlorobenzoic acid	20	30	82	121	Gerike et al., 1980
Formic acid	200	350	>1.5	>0.5	Englebrecht et al., 1957
	1,500	1,440	26	9.0	Sato et al., 1972
Valeric acid	200	350	>1.5	>3.0	Englebrecht et al., 1957
Caproic acid	200	350	>1.5	>3.3	Englebrecht et al., 1957
Heptanoic acid	200	350	>1.5	>3.5	Englebrecht et al., 1957
Benzoic acid	200	350	>1.5	>3.0	Englebrecht et al., 1957
Methyl cellulose	70	5,000	0.03	0.04	Blanchard et al., 1976
Pentachlorophenol	30	2,000	0.85	0.59	Kirsh et al., 1973
Aniline	20	10,000	0.18	0.57	Baird et al., 1977
Dimethylaniline	20	10,000	0.10	0.32	Baird et al., 1977
Chloroaniline	20	10,000	0.07	0.15	Baird et al., 1977
N,N-dimethyl-1-naphtylamine	20	10,000	0.02	0.06	Baird et al., 1977

[a] Assumed value.

[b] Actual measured COD value.

MASS TRANSFER IN AERATED WASTEWATER TREATMENT SYSTEMS

This section describes various equations used to estimate water-to-air mass transfer coefficients. Alternative equations are available in several situations (K_L for lagoons and settling basins; K_g for windswept sources). When alternative equations are available, the advantages and limitations are discussed. The various equations are summarized in Appendix A.

Available Equations

Hwang (1982) published an article describing reliable quantitative methods of estimating toxic emissions from land disposal facilities. This article provides many useful equations to estimate mass transfer coefficients. The following paragraphs describe some of the recommendations of this paper.

The overall rate of mass transfer, K_{OL} is predicted by combining the resistance of the liquid and the resistance of the gas.

$$K_{OL} = (1/k_L + 1/(Kk_g))^{-1} \quad (4)$$

where

k_L = the mass transfer coefficient for the liquid, g. mol/cm^2-sec

k_g = the mass transfer coefficient for the gas, g. mol/cm^2-sec

K = the partition coefficient, mole fraction gas/mole fraction liquid

K_{OL} = the overall mass transfer coefficient based on liquid concentrations, g. mol/cm^2-sec

This equation is valid for each of the aerated waste treatment processes previously described, with the exception of multiphase resistances (oil slick, surfactant layer). The resistance of an oil layer is relatively easy to predict, but in the case of volatile organic compound (VOC) release, the effect of surfactants is less well known. Effects such as electrostatic repulsion cannot be predicted without experimental data.

A modified equation for the overall mass transfer coefficient can be written as a modified form of Equation 3.

$$K_{fL} = \{(1/k_L) + [(\rho\delta)/(D_f MW_{ave} K_o)] + [1/(Kk_g)]\} \quad (5)$$

where

δ = thickness of film, cm

D_f = diffusion coefficient of VOC in oil, cm^2/sec

ρ = density of oil, g/cm^3

MW_{ave} = average molecular weight of oil, g/gmol

K_{fL} = film-liquid partition coefficient.

Equation 3 can also be modified to account for area modifying controls such as floating balls, etc. In any case, the equation for the controlled emissions should be a modified version of the uncontrolled emissions equation so that a common basis can be used for evaluating the control effectiveness.

Liquid Mass Transfer

The removal rate of VOCs in a flowing body of water after Cadena, et al., (1984) follows the equation:

$$\ln \frac{C}{C_o} = K_2 t \frac{K_{OL}^{ref}}{K_{OL}} = K_2 t \frac{D_{VOC}}{0.178} \tag{6}$$

where

K_2 = the oxygen reaeration rate constant in base e, sec^{-1}

C = the concentration of interest, mg/L

C_o = the initial concentration (at t = 0), mg/L

t = time, sec

D_{VOC} = the VOC diffusion coefficient, cm^2/sec

K_{OL}^{ref} = the overall mass transfer coefficient for a tracer, $g\text{-}mol/cm^2\text{-}sec$.

According to information presented by Metcalf & Eddy, (1972), rapids and waterfalls would have a K_2 value of >1.1/day. This would be similar to rates of mass transfer expected with some biological processes. Cadena et al. (1984) suggest a range of K_2 of 3.36 to 47.0 day^{-1} for rapid shallow streams (one foot deep). The value of K_2 is related to the depth of the stream by the power of 1.67 (Churchill, 1962) or 1.85 (Owens, 1964). Taking an intermediate value reaeration rate constants can be adjusted for different depths as follows:

$$\frac{K_2^{\text{ref}}}{K_2} = \left(\frac{h_{\text{ref}}}{h} \right)^{1.7} \qquad (7)$$

where

h = stream depth, cm.
h_{ref} = depth of reference stream, cm

The 30 cm (1 foot) depth of the shallow stream would suggest (by this relationship) that 300 cm (10 feet) deep streams would have lower values of K_2 by a factor of 50. This suggests that the values of Cadena are not inconsistent with those of Metcalf & Eddy (1972). For rapid agitation in a biotreatment system a value of K_2 of 17 day^{-1} is not unreasonable.

The value of the reaeration rate constant can also be estimated by a correlation of Owens et al. (1964) for stream flow velocities of 3-600 cm/sec.

$$K_2 = 50.5\, v^{0.67}/h^{1.85} \qquad (8)$$

where

K_2 = base e reaeration constant, hr^{-1}

v = velocity, cm/sec.

If a holding basin has a depth of 3 meters (10 ft) and a length of 10 meters (30 ft), with a residence time of 1.0 hour, the velocity would equal 0.28 cm/sec. This is less than the range of the correlation, and therefore, the estimate of K_2 is subject to increased uncertainty. Nonetheless, substituting into the above equation, the value of K_2 would equal $3.6(10^{-2})$ day^{-1}

Using the equation of O'Connor (1958) for a stream

$$K_2 = 12.9\, v^{0.5}/h^{1.5} \qquad (9)$$

where

v = velocity, ft/sec.

h = depth, ft.

The predicted K_2 for the holding basin would equal 0.038 day^{-1}.

These equations for flowing streams are not directly applicable to holding basins because the average velocity is less than the applicable range of the velocity in the equations, and the turbulence (due to the mixing of the influent) is not accounted for. The reaeration rate constant for holding basins would likely fall in the range between that of a sluggish stream (0.23/day) and that of a swift stream (1.15/day). A value appropriate for holding basins could be on the order of 0.5/day, which has been assumed for comparison purposes.

A typical mass transfer coefficient for benzene is approximately 7 × 10^{-5} gmol/cm^2-sec (see Table 17). Based upon a depth of 300 cm and a water molar density of 1/18 gmol/cm^3, the time constant of VOC decay from a surface impoundment would be 3 days. This value is not inconsistent with the stream reaeration rate constants (0.36/day vs. 0.5/day).

Another method of estimating liquid mass transfer coefficients is based upon wind friction. Mackay and Yeun (1983) suggest that the liquid mass transfer coefficient can be written as a function of the liquid velocity and the Schmidt number, where

$$k_L' = 1.0(10^{-6}) + 0.0144(U^*)^{2.2}(Sc_L)^{-0.5} \quad (10)$$

where

k_L' = liquid mass transfer coefficient, m/sec
U^* = $(U_{10})(6.1 + 0.63U_{10})^{0.5}/100$
U_{10} = air velocity 10 m above the surface, m/sec
Sc_L = liquid Schmidt number, dimensionless.

Equation (9) is valid where $U^* < 0.3$. Where $U^* > 0.3$, McKay and Yeun (1983) suggest,

$$k_L' = 1.0(10^{-6}) + 0.00341U^*(Sc_L)^{-0.5} \quad (11)$$

Assuming a wind velocity of 447 cm/sec (equivalent to 10 miles/hr), Sc_L = 1,000, U^* = 0.133 and $k_L' = 6.4(10^{-6})$ m/sec. The time constant for loss from the liquid would be estimated as:

$$\frac{0.0000064 \text{ m/sec}}{(3 \text{ meters depth})} \frac{3{,}600 \text{ sec}}{\text{hr}} = 0.0077 \text{ hr}^{-1} .$$

This calculated value of the time constant is equivalent to a mass transfer coefficient of 3.5 × 10^{-5} g·mol/cm^2-sec and is somewhat greater than the coefficients predicted by the correlations of Owens and Edwards (Table 17, 1.5 × 10^{-5} g·mol/cm^2-sec).

The estimated rate of volatiles loss from the relationship of Mackay (1983) is lower than that predicted from Churchill (1962) based on liquid flow only. It should be noted that the functionality (and therefore the predictions) of the equations of Churchill and Mackay are different. The absence of a functionality of depth of liquid may limit the applicability of the equation of Mackay for relatively deep bodies of water.

In some wastewater treatment facilities impellers or other devices are used to agitate the liquid surface. The entire tank may be agitated, or agitation may be carried out on only one portion of a body of water. A correlation for the mass transfer coefficient under agitation was presented by Thibodeaux (1978) where the mass transfer coefficient was proportional to the power of agitation and the square root of the ratio of the diffusion coefficient of the species to that of oxygen (Equation B, Appendix A).

In the case of liquid mass transfer without agitation from lagoons and other related facilities, the equation of Owens et al., (1964), and Gibbs (1964) can be useful (Equation C, Appendix A). The important variables in the Owens correlation are temperature, depth of the liquid, surface velocity, and the diffusion coefficient of the component of interest. The surface velocity is assumed to be the product of 0.035 and the wind velocity for a nonaerated surface or 0.03 m/s outside the effective aeration region for an aerated process. Values of liquid mass transfer coefficients calculated from the correlation of Owens, et al., (1964) are higher than those calculated from the correlation of MacKay and Yeun (1983).

Cohen, Cocchlo, and MacKay (1978) investigated the volatilization of benzene from water in the presence of wind waves. The mass transfer coefficient is a function of the roughness Reynolds number, which in turn is a function of the wind velocity and other parameters (Equation A, Appendix A).

The correlation is based on benzene in an unagitated system. The ratio of the diffusion coefficients between a species of interest and benzene is an important parameter which is used to extend their results to other components. Based on the work of Roberts and Dandliker (1983), the volatilization rate is proportional to the ratio of the diffusion coefficients to the 0.66 power. Although Cohen, Cocchlo, and MacKay (1978) discuss the theoretical basis for their correlation, it should be regarded as primarily empirical with some reservations as to its applicability to larger systems, such as lagoons.

The velocity of the surface away from the aeration region can be estimated by the correlation of Kullenberg (1976).

$$v = 0.3048\ (3.2809\ U/100)(1.506 + 1.5748\ U) \tag{12}$$

where

U = the velocity of the wind, m/s

v = the bulk velocity of the liquid, m/s

Mass Transfer from Falling Droplets

The air emissions from a falling droplet are of potential importance from a variety of wastewater treatment sources. Some important aspects of droplet emissions are (1) the mass transfer coefficients are substantially greater in falling droplets than from surfaces and (2) some of the droplets may never reach the earth. As the droplet loses water by evaporation, its velocity decreases. Eventually some of the droplets may evaporate to dryness, forcing all of the pollutants (VOCs, semivolatiles, non-volatiles, inorganics) to be emitted into the atmosphere, either as vapors or aerosols. There will be very little biological decay during the short time of droplet fall. The sources which produce falling droplets include roughing filters, spray ponds, and cooling towers.

Lenard (1921) reported that a droplet could not fall faster than 8 m per second and this maximum droplet velocity is known as the terminal velocity. The droplet forms an inverted cup and breaks up at the higher velocities. A free falling droplet (without wind resistance) would require approximately 0.8 seconds to achieve this velocity. The travel distance would be 3.1 meters, a distance comparable to that present in many wastewater treatment systems employing spray ponds.

The rate of droplet fall can be estimated by means of a general equation for the terminal velocity, v_t of spheres (McCabe and Smith, 1967).

$$v_t = \left[\frac{4\ A_e\ D_p^{1+n}\ (\rho_p - \rho)}{3\ b_1\ \mu^n\ \rho^{1-n}}\right]^{1/(2-n)} \tag{13}$$

where

$$A_e = (Re_p)^{2-n}\ \frac{3\ b_1 \mu^2}{4\ \rho(\rho_p - \rho)} \tag{14}$$

The values of b_1 and n depend on the values of the particle Reynolds number, Re_p, which is calculated as:

$$Re_p = \frac{D_p v_t \rho}{\mu} \tag{15}$$

where

D_p = the particle diameter, cm

ρ = density of air, g/cm^3

ρ_p = density of droplet, g/cm^3

μ = viscosity of the air, g/cm-sec.

The necessary constants are given in Table 14 for three specific ranges of Reynolds numbers. The Reynolds number is calculated iteratively on the basis of an assumed velocity. The velocity is then calculated and a corrected Reynolds number is obtained.

The overall mass transfer coefficient for a falling drop can be calculated (Treybal, 1968) as,

$$K_{OL} = Sh_{av} C D_{AB} / D_p \qquad (16)$$

where

D_{AB} = diffusion coefficient of the compound in water, cm^2/sec

C = concentration, gmol/cm^3

and

$$Sh_{av} = Sh_o + 0.347[Re_p(Sc)^{0.5}]^{0.62} \qquad (17)$$

where

Sc = Schmidt number = $\mu/(\rho D_{AB})$

and

$$Sh_o = 2.0 + 0.569(GrSc)^{0.250} \qquad (18)$$

In cases where,

$ScgD_p^3\rho^2/\mu^2 > 10^8$

Equation (18) should be used instead of Equation (17):

$$Sh_o = 2.0 + 0.0254(Gr)^{0.333}(Sc)^{0.577} \qquad (19)$$

where

Gr = Grashof number = (980 cm/sec^2)$D_p^3\rho^2/\mu^2$.

TABLE 14. CONSTANTS FOR DRAG COEFFICIENT CALCULATION

Re_p range	b_1	n
$Re_p < 2$	2.4	1
$2 < Re_p < 500$	18.5	0.6
$500 < Re_p < 200{,}000$	0.44	0

SOURCE: McCabe and Smith, 1967.

This equation is similar to the relationship proposed for mass transfer from a sphere in a packed bed (Wakao and Fanayku, 1978). The velocity due to porosity of the bed would account for some of the differences in the two equations.

$$Sh_{av} = 2 + 1.1\ (Re_{p}\ Sc^{5})^{0.6} \tag{20}$$

When the velocity of a falling drop can be estimated, the mass transfer coefficient can be estimated. Both mass transfer for water and VOCs should be calculated, since the droplet can evaporate to dryness before reaching the earth. Treybal (1968) states that spray ponds are subject to high windage losses of water. Cooling towers have mist eliminators which can reduce some of the windage.

Table 15 presents the results of a numerical simulation of the VOC loss from a falling droplet using the equation suggested by Treybal (1968). Small droplets readily lose their VOC components into the atmosphere and larger droplets lose significant amounts of VOCs over a relatively short distance of travel. In addition, the mass transfer of water away from the droplet surface is relatively rapid, with small droplets evaporating to dryness after several meters fall (see Table 16).

Thin Falling Films

Evaporation from cooling towers occurs from a thin falling film of liquid. The film Reynolds number is defined as:

$$Re_{f} = 4\Gamma/\mu$$

where

Γ = the mass flow rate of liquid per unit film width, g/cm-sec.

The film thickness, δ (cm), can be determined as follows:

$$\delta = \left(\frac{3\mu\Gamma}{\rho^{2} g_{c}} \right)^{1/3} \tag{21}$$

where

g_{c} = gravitational constant ≅980 cm/sec^{2}.

The overall mass transfer coefficient (for $Re_{f} > 100$) is

$$\frac{K_{OL}\delta}{D_{AB}} = Sh_{av} = \left(\frac{3}{2\pi} \frac{\delta}{L} ReSc \right)^{\frac{1}{2}} \tag{22}$$

TABLE 15. FRACTION OF BENZENE REMAINING IN A DROPLET FALLING AT TERMINAL VELOCITY

Falling distance (m)	Initial droplet diameter		
0	0.1 cm	0.2 cm	0.5 cm
0.21	0.04		
0.68		0.47	0.80
1.36		0.21	0.71
1.60		0.18	0.68
2.03		0.10	0.60
2.67			0.53

TABLE 16. TOTAL DISTANCE FALL BEFORE EVAPORATION TO DRYNESS

Initial diameter (cm)	Distance (cm)
0.05	350
0.10	1500

where

L = length of column (or section thereof), cm.

For $Re_f < 100$, $Sh_{av} \cong 3.41$.

Mass transfer in falling films, such as those present when wastewater flows over a clarifier weir, can be considered by the method of Owens (1964), modified for 90 percent less turbulence in free fall as opposed to continuous shear against a vertical surface. An example is presented in Appendix B, part IIIc. The gas phase mass transfer is estimated by the correlation of MacKay and Yeun (1983). The falling film is considered as plug flow (well-mixed perpendicular to the direction of fall). This approach can be considered a semi-empirical one, since the value of the multiplier applied to the correlation of Owens, (0.1) can be adjusted as additional experimental data are obtained.

Gas Mass Transfer

The classic approach to predictions of mass transfer coefficients, (Sherwood & Pigford, 1952), is presented in Equation H for comparison purposes. The exponent of the diffusion coefficient in Equation H (Appendix A) agrees roughly with the recent work of Roberts and Dandliker (1983); this suggests the possiblity that the mass transfer mechanisms are similar, whether they are for the turbulent gas-phase or the turbulent liquid-phase transfer processes. It is also interesting to note that the classical methods predict mass transfer coefficients that are similar to those observed in recent research. It should be noted however, that the exponents in some of the recent correlations differ from those used in the Colburn equation (Sherwood and Pigford, 1952).

Equation I (Appendix A), from Thibodeaux and Parker (1974), predicts the gas-phase mass transfer coefficients from surface impoundments where the gas mass transfer coefficient is a function of the wind velocity, the diffusion coefficient, and the length of the impoundment. For the case where the liquid surface is agitated, the gas-phase mass transfer coefficient can be estimated from the correlation of Rinehart (1977). The gas mass transfer coefficients are a function of the system geometry and various dimensionless numbers describing it.

In general the more recent correlations are similar to the classic equation (Sherwood and Pigford, 1952). Considering the thickness of the boundary layer in turbulent flow in circular conduits, the classical equations for turbulent flow should be applicable to planar systems; moreover, some of the more recent correlations lack the extensive experimental support that the classical equations have. It is recommended that the Colburn type equation (Equation H, Appendix A) be used for the gas phase transfer from surfaces.

Mackay and Leinonen (1975) concluded that the mass transfer resistance of the gas phase is negligible for evaporation of volatiles. For semivolatiles ($H < 0.0001$ atm M^3/mol) the gas phase mass transfer resistance can be significant. Their conclusions were based upon reported values of the gas phase mass transfer coefficient of 3000 cm/hr (0.05 g mol/cm^2-sec). This is substantially greater than the liquid phase mass transfer coefficient in unagitated systems, and for situations where $K > 1$, the liquid film resistance would likely control the rate of mass transfer.

Mackay and Yeun (1983) recommend the following gas phase mass transfer coefficient.

$$k_g' \text{ (m/s)} = 0.001 + 0.000462\, U^* \, Sc_g^{-0.67} \tag{23}$$

where

$U^* = (6.1 + 0.63\, U_{10})^{0.5}\, U_{10}/100$

U_{10} = wind velocity at 10 meters, m/sec

Sc_g = gas Schmidt number [viscosity/(density × diffusion coefficient)]

This correlation predicts lower mass transfer rates than the Reinhart equation (Equation J, Appendix A). The Reinhart equation should predict rates higher than those from the Mackay equation since there should be greater mass transfer associated with splashing and mechanical agitation than from wind agitation alone. Thus, the equation of MacKay and Yeun (1983) is recommended for wind agitated systems while the Reinhart equation is preferred for mechanically agitated systems.

Table 17 presents a summary of the results from using various equations to predict the mass transfer coefficients from a clarifier. In general, the more recent correlations show close agreement for both gas and liquid phase resistances.

TABLE 17. A COMPARISON OF SELECTED PREDICTIONS OF MASS TRANSFER COEFFICIENTS FOR BENZENE EMISSIONS FROM A CLARIFIER
(Model Plant 1, Wind Velocity 447 cm/sec)

Gas phase coefficients [g mol/(cm^2 sec)]	
"J factor" type (Sherwood and Pigford, 1952)	2.2×10^{-5}
Mackay and Matsuga (1973)	3.1×10^{-5}
Thibodeaux and Parker (1974)	1.7×10^{-5}
Mackay and Yeun (1983)[1]	2.2×10^{-5}
Reinhart (1977)[2]	18.0×10^{-5}
Liquid phase coefficients [g mol/cm^2 sec]	
Owens, Edwards, and Gibbs (1964)	6.1×10^{-5}
Cohen, Cocchlo, and Mackay (1978)	7.2×10^{-5}
Owens (1964)	4.9×10^{-5}
Mackay and Yeun (1983)[1]	3.5×10^{-5}
Metcalf and Eddy (1972)[3]	5.0×10^{-5}

[1] wind agitation of surface.
[2] area away from mechanical agitation, in aerator.
[3] assumptions in text of this report.

Subsurface Aeration

The mass transfer into a bubble is often viewed from the perspective of the liquid: the change in concentration of the liquid is modeled. From the perspective of air emissions, the concentration in the off-gas is of importance. Since a close approach to equilibrium is expected, the overall mass transfer coefficient for the liquid cannot be used to calculate the bubble concentration under a variety of conditions.

As bubbles rise through wastewater containing VOCs, the rate controlling mechanism for the flux of VOCs into the bubble is controlled by the liquid mass transfer resistance. The liquid mass transfer coefficient, K, is predicted by the relationship of Calderbank (1967).

$$K_L(Sc)^{0.5} = 0.42\ \mu_{air}^{0.33} \tag{24}$$

Simulation of bubble rise using the above relationship indicates that the mass transfer is controlled by the liquid phase resistance and that equilibrium is achieved rather quickly.

This theoretical prediction was confirmed experimentally. Smith (1980) has shown that the rate of loss of VOC is controlled by the liquid phase resistance, except for low volatility compounds. Truong and Blackburn (1984) demonstrated that the rate of stripping in a dispersed bubble system could be predicted closely by equilibrium considerations: that is, the bubble system was approximately equilibrium controlled, not mass transfer controlled. Their equation was of the following form:

$$K_{OL}'a\ \ V/Q = 0.00371\ H^{1.045} \tag{25}$$

where

$K_{OL}'a$ = stripping rate constant (hr-1)
V = volume of liquid (L)
Q = air flow rate (L/hr)
H = Henry's law constant (torr L/g-mole)

This relationship is based on toluene, MEK, 1,4-dichlorobenzene, and phenol in water, so the data encompasses semi-volatiles as well as volatiles. In addition, the predicted kinetics agree well with various reported literature data (Truong and Blackburn, 1984) further substantiating the concept that dispersed bubble strippers are an equilibrium process.

The diameter of a bubble produced by a subsurface aerator is a function of the power input to the aerator. Using Calderbank's correlation (Freeman, 1981):

$$D_b = [4.15(ST)^{0.6} (PI/V)^{-0.4} (\rho_L)^{-0.2} g_{hf}] + 0.09 \qquad (26)$$

where

D_b = bubble diameter, cm

ST = surface tension, g/cm

PI/V = power input per basic volume, g-cm^2/(cm^3-sec)

g_{hf} = gas holdup fraction = v_g/v_b

v_g = superficial gas velocity, cm/sec

v_b = actual bubble velocity, cm/sec.

The ratio of the stripping rate constant of volatile hydrocarbons and chlorinated hydrocarbons to the oxygen reaeration rate constant in a bubble system was found to be proportional to the square root of the ratio of the critical volume of oxygen to the critical volume of the volatile compound. For more spherical molecules, the ratio of stripping rates was proportional to the cube root (Matter- Muller, 1980). The system used in this study may have been small enough for the process to be kinetically controlled.

The rate of stripping is generally equilibrium controlled except for very highly volatile compounds; the gas in the rising bubbles would be saturated with the VOCs in the water. The rate of loss of VOCs into the atmosphere can be predicted by a relationship such as that recommended by Blackburn and Truong (1984). The major data required would be the VOC concentration in the aerated water, the gas flow rate, and the equilibrium partition constant (Henry's constant).

Although most compounds are expected to reach equilibrium within the bubbles before the bubbles reach the surface, the concentrations of highly volatile materials in the bubbles such as vinyl chloride and oxygen are expected to be kinetically controlled. The mole fraction of these compounds in the gas phase is large compared to the mole fraction in the liquid phase. Therefore, the liquid phase resistance and bubble residence time in the liquid determine the concentration. For these volatile compounds, the concentration can be estimated by specifying the bubble size, calculating the rate of bubble rise, estimating the liquid mass transfer coefficient with an appropriate correlation (Calderbank, 1967), and numerically integrating to obtain the concentration within the bubble as a function of time. Providing smaller bubbles and a longer rise distance promotes the approach to equilibrium.

Mass transfer in a bubble column was investigated by Munz (1982) and the mass transfer was related to the Henry's constant for a series of VOCs. The overall mass transfer coefficient for stripping (of five chlorinated hydrocarbons) was found to be linearly related to the overall mass transfer coefficient for oxygen absorption over a wide range of operating conditions.

Roberts and Dankliker (1983) caution against using the assumption of liquid phase resistance control in laboratory studies. They suggest that the gas phase resistance may be important based on laboratory studies with chloroform, and that the gas phase resistance may be important in mechanically agitated liquids.

The data of Truong and Blackburn (1984) agree well with the concept of equilibrium being established rapidly in bubble columns. In a benzene stripping experiment they observed a stripping rate constant of 1.13 hr^{-1} with 2 L/min air flow through a liquid volume of 25.7 liters. The corresponding value of H is calculated as follows:

$$\frac{(25.7\text{ L liquid})(1000\text{ g/L})(24.0\text{ L/mol})(1.13/\text{hr})}{(2\text{ L gas/min})(60\text{ min/hr})(18\text{ g }H_2O/\text{mol})} = 323$$

This compares to a reported value of Henry's constant for benzene, of 295 (Freeman, 1982). It is interesting to note that surfactants and biomass tend to depress the Henry's constant for toluene, but for 1,4-dichlorobenzene, the addition of biomass and surfactants did not depress the Henry's constant.

Table 18 illustrates the rapid approach to equilibrium of air bubbles rising in water. Bubbles produced by fine diffusers are on the order of 0.1 cm in diameter. Except perhaps for large bubbles in laboratory equipment, equilibrium can be assumed for VOC absorption from water. The same assumption for oxygen uptake by the water is not necessarily valid. Small bubbles sparged into the water would theoretically tend to maximize oxygen absorption while controlling VOC loss.

TABLE 18. CONCENTRATION OF BENZENE ABSORBED DURING BUBBLE RISE IN WATER (mole fraction)

Bubble size (cm)	0.1	0.3	0.6
Concentration, Equilibrium	0.03	0.03	0.03
Concentration (0.1 sec)	0.0236	0.012	0.0068
Rise distance (cm) at 0.1 sec	1.1	3.0	4.2
Concentration (0.2 sec)	0.0286	0.0193	0.012
Rise distance (cm) at 0.2 sec	2.22	6.0	8.4
Concentration (0.4 sec)		0.0261	0.0193
Rise distance (cm) at 0.4 sec		12	16.86
Concentration (1.0 sec)			0.0277
Rise distance (cm) at 1.0 sec			42.1

ADSORPTION

Organic compounds can be removed from wastewater by adsorption on surfaces. Potentially adsorptive surfaces include suspended solids present in the wastewater, soil in unlined surface impoundments, polymeric liners in lined surface impoundments, tank walls of steel or concrete, and biomass generated from decomposition of organic compounds.

With the exception of the suspended solids and suspended biomass, adsorptive surfaces will rapidly reach equilibrium with wastewater of constant composition. Once the surfaces are "loaded," no further net adsorption will take place. The biomass or secondary sludge stream removed from the treatment system may be enriched in VOCs with respect to the effluent wastewater. In an activated sludge system, a waste sludge stream that is about 1 percent dry solids is removed from the process. Upon dewatering, the sludge may become more concentrated in certain organics than the water which was removed from it.

In absolute terms, the importance of adsorption on sludge as a pathway for removal of VOCs from the system is decreased by the relatively low percentage of total solids in the sludge. About 99 percent of the mass of the sludge is water; the VOC content of this water is approximately that of the bulk liquid (in a completely mixed system this concentration is approximatley that of the effluent). Thus, if the solids in the sludge were enriched 100-fold in VOCs with respect to the wastewater, the resulting sludge stream would still have a VOC content of only about twice that of the solids-free wastewater.

Estimation of the partition coefficient of VOCs between sludge solids and water can be based on the octanol-water partition coefficients for specific compounds as reported by Hansch and Leo (1979). Matter-Muller et al. (1980) determined that a linear relationship exists between the log of the octanol-water partition coefficient and the log of the distribution coefficient between activated sludge solids and the aqueous phase. This relationship was observed for chlorinated aromatic compounds, but on a theoretical basis it implies that the sludge solids act similarly to an immiscible organic phase in equilibrium with water. In the absence of data from direct measurements for the specific compounds of interest, it may be assumed that the following relationship, described by Matter-Muller et al. (1980), is valid:

$$\log K_{s,y} = 0.67 \log P_{ow} - 2.61 \quad (27)$$

where

$K_{s,y}$ = concentration of VOCs in sludge solids/concentration of VOCs in wastewater [(mg/kg)/(mg/m^3)]

P_{ow} = concentration of VOCs in octanol/concentration of VOCs in water.

PREDICTIVE FATE MODELS

The removal mechanisms can be divided into three pathways: (1) adsorption, (2) evaporation or air-stripping, and (3) chemical and biological oxidation. Chemical and biological oxidation is treated as one pathway due to the difficulties in experimentally differentiating between the two mechanisms.

Structure-activity correlations have been developed by Strier (1983, 1985) in an effort to predict the relative importance of each removal pathway in activated sludge systems. By grouping compounds according to their ability to adsorb on activated carbon, and considering their solubilities, molecular weights, chemical structure and other similarities, Strier formed six "clusters" of compounds. Table 19 lists examples of chemicals found in each cluster. Table 20 gives a general description of the chemical and physical properties that were used as a basis for the grouping of each cluster.

By using data obtained from field tests at publicly owned treatment works and pilot studies conducted at EPA, Strier developed empirical equations to predict the percent removal of an organic compound by adsorption and by air-stripping in a well-aerated activated sludge treatment system. These equations are presented in Table 21. The appropriate equation to use for each cluster is also outlined in Table 21, though there is some question as to which air-stripping equation to use for Cluster V compounds. For those compounds in Cluster V which are not particularly amenable to biodegradation or have a high Henry's law constant (i.e., greater or equal to the Henry's law coefficient, H, of benzene), Equation 3 should be used. For those Cluster V compounds which are biodegradable and/or have a moderate-to-low Henry's law constant (i.e., H < H of benzene), Equation 4 should be used. Obviously, the most important parameters are the log octanol-water partition coefficient (log P_{ow}) and the Henry's law constant. Even without % metabolized data, Equation 4 could still be used to estimate the % removal by air-stripping since the dependence of Equation 4 on the % metabolized term is small.

TABLE 19. CLUSTERS: EXAMPLES OF THEIR COMPOUNDS AND FATE DESCRIPTION
(Strier, 1982)

Cluster	Example compounds	Mol. wt.	Fate description
I	Hexachlorobenzene 2,3,7,8-TCDD PCBs	284.8 332 275-420	These are among the most incompatible and least soluble organic pollutants. They are removed to at least 70% in primary and secondary sludges, with little air emissions.
II	N-Nitrosodimethylamine 1,2-Benzanthracene Pyrene	74.1 228.3 202	These compounds are essentially nonbiodegradable with little air emissions. They are adsorbed by primary and secondary sludges to the extent of 70%.
III	1,2,4-Trichlorobenzene Hexachlorocyclopentadiene Anthracene Fluorene	181.5 273 178.3 152.2	These compounds are biodegradable up to 50%. They are adsorbed up to 50-60% by combined primary and secondary sludges. There is little air stripping of these compounds, except for hexachlorocyclopentadiene, which is potentially highly air-strippable.
IV	Benzidine 1,4-Dichlorobenzene Hexachlorobutadiene 4,6-Dinitro-0-cresol	184.2 147 260.8 198.1	These compounds are mostly biodegraded with the exception of the highly chlorinated compounds. Removal by adsorption on combined primary and secondary sludges is no better than 30%. The butadiene is capable of being highly air-stripped and is also highly chemically reactive.
V	Benzene Carbon tetrachloride Chlorobenzene 1,1,2,2-Tetrachloroethane 1,2- & 1,3-Dichlorobenzene Nitrobenzene Phenol Tetrachloroethylene	78.1 153.4 112.6 167.9 147 123.1 94.1 165.8	These compounds are adsorbed on sludges by less than 25%. The highly chlorinated compounds in this cluster will be air-stripped. The phenols will be highly biodegraded, while the benzenes will be preferentially air-stripped.
VI	Acrolein 1,2- & 1,1-Dichloroethane 1,1,1-Trichloroethane 1,1,2-Trichloroethane Chloroform Methylene chloride Trichloroethylene Vinyl chloride	56.1 99.0 133.4 119.2 119.2 84.9 131.4 62.5	Compounds in this cluster are essentially not adsorbed on primary or secondary sludges. These compounds are essentially not biodegraded, except for acrolein. Compounds in this cluster are removed primarily by air-stripping.

TABLE 20. CLUSTER CHARACTERISTICS USED AS A BASIS IN GROUPING COMPOUNDS (Strier, 1982)

Cluster	Cluster characteristics[a]
I	ETEL 1.0 μg/l; water insoluble; log P_{ow} range of 5.6-7.7; high molecular weights (250-350); nonbiodegradable; nonvolatile; melting point range of 440-570 °K.
II	ETEL = 1 - 10 μg/l; low water solubility; generally lower molecular weights and melting points than cluster I; nonbiodegradable; nonvolatile.
III	ETEL = 10 μg/l; increasing solubility and biological activity over cluster II; log P_{ow} range of 3.0-5.3; mid-range molecular weights (150-275); mostly low volatilities.
IV	ETEL = 25 μg/l; increased water solubility: log P_{ow} range of 1.5-3.5; typically biodegradable; mid-range molecular weights (150-260); high boiling points/low volatility.
V	ETEL = 50 μg/l; log P_{ow} range of 1.5-3.0; mostly liquids at ambient temperatures; molecular weight range fo 80-1801 typically biodegradable; lower boiler points and increased volatility than cluster IV.
VI	ETEL = 100 - 1,000 μg/l; low log P_{ow} (0-2.5); low molecular weights (50-170); only slightly biodegradable; high Henry's law constant/volatile/low boiling point.

[a] ETEL is the estimated effluent concentration, assuming an influent concentration of 1 mg/l, from an activated carbon column. This is the primary basis for developing the clusters.

TABLE 21. EQUATIONS FOR ESTIMATING FATE OF ORGANIC PRIORITY POLLUTANT COMPOUNDS (Strier, 1985)

	Function[a]	For cluster(s)	Equation
1.	% Ads. vs. log P_{ow}	I-IV if Eqn. 1 % Ads. >70%	% Ads. = 14.1 log P_{ow}
2.	% Ads. vs. MW + MP + log P_{ow}	I-VI if Eqn. 1 % Ads. <70%	% Ads. = 28.2 - 0.01 MP + 0.05 MW + 14.1 log P_{ow}
3.	% Air-strip. vs. H + log P_{ow}	V-VI	% Air-strip. = 8.8 + 10.8 H + 9.8 log P_{ow}
4.	% Air-strip. vs. H + log P_{ow} + % metabolized	III-V	% Air-strip. = -6.1 + 1.5 H + 3.5 log P_{ow} 0.07 % metabolized

[a] Abbreviations:
MW = Molecular weight (g/mol)
MP = melting point (°K)
H = Henry's law constant (Atm-m^3×1,000/mol)
P_{ow} = Octanol-1/water partition coefficient

[b] Refers to experimentally determined fraction of compound biodegraded.

The predicted fate of compounds according to their clusters is given in Table 22. Note that, in general, each cluster has its own characteristic removal pathways. This allows useful generalizations to be drawn about a compound's fate knowing only the cluster number to which it belongs. Furthermore, the ability to make more accurate predictions about the fate of an organic pollutant using a limited number of known parameters and the mathematically simplistic equations of Table 21 is a great advantage of the structure-activity correlations.

Although Strier does not present any equations which allow the prediction of percent removal by biochemical oxidation, he does outline some useful generalizations. Compounds which have intermediate solubilities (log P_{ow} = 1.5-3.5) are excellent candidates for biochemical oxidation. Compounds which have a log P_{ow} value greater than 3.5 tend to be insoluble and are readily adsorbed on sludge. Compounds which have a log P_{ow} value of less than 1.5 are often volatile. Thus, compounds with a low log P_{ow} and a high Henry's law constant are typically air-stripped.

Even though a compound is soluble in water and nonvolatile, there is no guarantee that it can or will be biodegraded. That is, there are chemical structures and specifically chemical substituents that greatly inhibit biochemical oxidation. These substituents are electron-attracting in nature and are referred to as electrophilic. Examples of these are the halogens (Cl, Br) and nitro (NO_2) and nitrosamine (>N-N=O) groups. Their presence on an organic compound reduces that compound's ability to be biodegraded. Further substitution of these electrophylic groups on an organic compound further reduces its ability to biodegrade.

Conversely, presence of a nucleophylic or electron-donating substituent will enhance biochemical oxidation. Examples of these functionsl groups are hydroxyl (-OH), amino ($-HN_2$), methyl ($-CH_3$), and ethyl ($-C_2H_5$) groups. Unlike the electrophylic substituents, further addition of a nucleophylic substituent has little additional effect on biochemical oxidation rates. However, multiple nucleophylic substituents on an organic compound typically enhance that compound's reactivity. In the presence of both nucleophylic and electrophylic functional groups, the compound is usually biodegradable or at least chemically reactive.

TABLE 22. PREDICTED FATE OF ORGANIC COMPOUNDS ACCORDING TO CLUSTER NUMBER (Strier, 1982)

Cluster	% sludge	% biodeg.	% air
I	<80	0	0
II	>70	0	0
III	50	50	0
IV	30	<70	0
V	0-25	0-96	0-100
VI	0-5	>0	100

Even though the structure-activity correlations are simple and often accurate, they are not without their limitations. As stated previously, no equation was presented by Strier to determine the percent removal by biochemical oxidation. It was assumed that the rate of either adsorption or air-stripping was much faster than that of biochemical oxidation. Although this is typically the case, the structure-activity correlations may not be predictive when the rate of biochemical oxidation competes with the rate of adsorption or air-stripping. Furthermore, the equations presented were developed from data of well-aerated activated sludge treatment systems. Consequently, due to the empirical nature (or lack of theoretical backing) of the equations, they may be of questionable validity for predicting the fate of organic pollutants in different aerated treatment facilities (i.e., trickling filters, aerated lagoons, evaporation ponds, or even activated sludge systems operating under different process conditions than those at which the data had been collected and the equations fitted). Nonetheless, the structure-activity correlations presented give remarkably accurate fate predictions for a number of organic compounds. Also, Equation 4 can be used for Clusters III-VI to predict the decreased removal by air-stripping under conditions of less aeration.

The equations presented by Strier (1982, 1985) can give good estimates on the importance of air and adsorption removal mechanisms for well-aerated activated sludge treatment facilities. This approach may also be employed to predict pollutant fates for different aerated biological treatment systems, however, this may necessitate the development of different empirical equation coefficients.

SECTION 5

MATHEMATICAL MODELS FOR AERATED WASTE TREATMENT

SELECTION OF MODELS

This section describes mathematical models which are recommended for estimating instantaneous air emissions from aerated waste treatment processes. Aerated waste treatment includes the following processes:

- Lagoons
- Clarifiers
- Dissolved air floatation (DAF)
- Surface aerators
- Diffused air
- Trickling filters
- Agitated holding tanks
- Spray ponds
- Cooling towers

These aerated waste treatment processes are expected to encompass most of the air emission sources associated with wastewater treatment technologies employed at hazardous waste management facilities.

The models of the wastewater treatment processes can be formulated by combining equations for each of the physical phenomena which control the release of pollutants into the atmosphere. The equations for the significant phenomena which govern the various mass transfer mechanisms include the following:

A. Liquid phase resistance in a body of water
B. Liquid phase resistance in an agitated system
C. Liquid phase resistance in a flowing film
D. Liquid phase resistance in a droplet
E. Liquid phase resistance around a rising bubble
F. Gas phase resistance over a surface
G. Gas phase resistance over an agitated surface
H. Gas phase resistance over a falling droplet
I. Gas phase resistance in a rising bubble
J. Gas phase resistance over a flowing film

Parameters that are required for calculation of the mass transfer rate include the following:

1. Surface area
2. Flow rate of liquid
3. Liquid volume

4. Flow rate of gas
5. Equilibrium partitioning into gas
6. Biological decay rates
7. Adsorption partitioning into biomass
8. Residence time
9. Fraction of the surface agitated
10. Fraction of drops lost in drift.

The required models for the aerated waste treatment processes include the following combination of equations and parameters:

Lagoons	A, F, 1, 3, 4, 5, 6
Clarifiers	A, F, 1, 2, 3, 4, 5, 6, 7
DAF	E, F, I, 1, 2, 3, 4, 5, 6, 7
Surface aerators	A, B, F, G, 1, 2, 3, 4, 5, 6, 7, 9
Diffused air	D, I, 2, 3, 4, 5, 6, 7
Trickling filters	C, D, H, J, 1, 2, 4, 5, 6, 7, 8, 10
Agitated holding tanks	B, G, 1, 2, 3, 4, 5, 6, 7
Spray ponds	A, D, F, H, 1, 2, 3, 4, 5, 6, 7
Cooling towers	C, D, J, H, 1, 2, 4, 5, 6, 7, 8, 10

The equations and parameters are not inclusive of all potentially important elements and the list above includes elements that may not be important. For example, the biological decay during a droplet fall is negligible.

In general, the following equations are available for predicting the flux of volatiles from all of the above mass transfer mechanisms except liquid phase resistence in a flowing film or droplet and gas phase resistence in a rising bubble. Many of the parameters which characterize waste treatment facilities can be assumed, estimated, or measured at specific facilities. The equilibrium partitioning into the vapor phase can be estimated within ± 30 percent. The biological decay rates are even more variable and uncertain.

When a process has zones of distinctly different emission rates, it is possible to estimate the individual rates from the different zones. The concentration of the VOCs may be different in the different zones, and the rate of change of concentration can be radically different in the different zones. In this case, a method of predicting the exchange of liquid between the different zones must be established to model transient effects.

There are various models which can be used to estimate mass transfer rates from aeration sources. These models vary in complexity and the type of information required for establishing input parameters. Levels of model complexity are presented in Table 23, in order of increasing complexity. Models with a complexity level of 1 form the basis of emissions estimation

TABLE 23. MODEL DATA REQUIREMENTS

Complexity level of model	Waste Input	Weather	Source Characteristics	Operation
1	E1	E1	E1	E1
2	E2	E1	E3	E1
3	M1	E2	M1	E3
4	M2	E2	M2	M1
5	M3	M2	M3	M2

E1 = estimated
E2 = estimated using a survey of existing data
E3 = estimated from site questionnaires
M1 = measured on site
M2 = measured over a period of time on site
M3 = measured at different times and locations.

using only limited data; Models with a complexity level of 5 predict detailed transient emissions from various areas of specific facilities. Operating conditions at one specific site may vary considerably from day-to-day and from month-to-month. Data representing one specific time at a specific site may be useful in estimating the validity of the model.

The level of model complexity selected depends on several factors:

1. Regulatory needs
2. Resources available to collect data
3. Equations/methodology available to analyze the data.

In general, the level of model selected should not be limited by the computational complexity of the calculations and data analysis since this can be done by computer. However, theoretical methods are not available to perform the calculations necessary for the most complex models (e.g., level 5 models, Table 23). In the discussion that follows the influence of the second and third factors on data collection and model choice is considered. Regulatory needs will not be discussed in this report but may influence the ultimate selection of a model.

Pretreatment

Pretreatment, including bar screens and grit chambers, removes sand, grit, and other items from the waste stream. Since there is little mixing, the pretreatment process is modeled as a "plug flow" system: the wastewater flows across the vessel, losing some of the volatiles as it proceeds. The loss of VOCs from the unit is the integral of the loss from an "average" element of the waste as it flows through the pretreatment process with time. The "average" time an element is retained in the pretreatment process is:

$$\tau = V/Q \tag{28}$$

where

V = volume of pretreatment unit, m^3

Q = volumetric flow rate, m^3/sec.

The rate of decrease in mole fraction, X, of a given compound is:

$$\frac{dX}{dt} = - \frac{K_{OL}aX}{\rho'_m} \tag{29}$$

where

K_{OL} = overall mass transfer coefficient, g mole/cm^2-sec

a = interfacial surface area, cm^2/cm^3

ρ'_m = molar density, g mole/cm^3.

Substituting (A/V) for a , where A and V are the surface area (cm^2) and volume (cm^3) of the treatment unit and integrating yields:

$$\ln(X_{out}/X_{in}) = -K_{OL}A/(10^6\ Q\rho'_m)\ . \tag{30}$$

The fraction of VOC lost in the process, F is given by

$$F = 1 - \exp[-K_{OL}A/(10^6\ Q\rho'_m)] \tag{31}$$

The values of A and Q can be estimated for the actual plant or obtained from a model plant. Either the individual values or the ratio A/Q is sufficient. The molar density of water ρ'_m is assumed to be (1/18 g-mol/cm^3). The value of K_{OL} is waste specific and depends on the value of the gas mass transfer coefficient, the liquid mass transfer coefficient, and the partition coefficient (see Equation 4). The diffusion coefficients are VOC compound specific, and the partition coefficients are both VOC compound specific and waste specific.

The gas phase coefficient is estimated by the correlation with wind speed of Mackay and Yeun (1983, Equation H, Appendix A). The liquid phase resistance may be estimated by several techniques.

1. assume that the liquid phase resistance is zero
2. use a flowing stream model
3. use an assumed mixing rate

Because there are few experimental data to support approach 3 and approach 1 is inaccurate for many compounds, approach 2 will be used based upon the equation of Owens et al. The partition coefficient is unknown but will be estimated using Henry's law for single components in water.

Clarifiers

Clarifiers are designed to remove suspended solids and thus the solids concentration increases with depth. Concentrations of dissolved VOCs are not expected to vary significantly with depth. The "plug flow" model will be used, as given in Equation (29). Equation 31 is applicable to the fraction of each VOC lost in the clarifier. The primary clarifier is assumed to have no microorganisms present, and consequently, no biodegradation is occurring. The gas mass transfer coefficient is estimated by the correlation of Mackay and Yeun (1983) given in Equation 23. The liquid mass transfer coefficient is based upon the correlation of Owens et al. (1964). The values of mass transfer coefficients from the correlation of Owens et al. are substantially greater (400%) than other predictions, (MacKay, 1983; Owens, et al. 1964). However, since the induced turbulence at the entrance to the clarifier can lead to higher rates of mass transfer than would be present in a stagnant system, such an inflated predictor may be justified for clarifiers. As observed from the apparent agreement of the model (see detailed calculation in Appendix B) with the reported losses of VOCs from clarifiers which follow, there is little to suggest that the predictions can be improved with a different equation.

The flow of water out of the clarifier occurs around the perimeter of the vessel creating a thin film of water. A modified form of the Owens' equation was used to model the VOC lost from this waterfall. Since the flow is freefall in air and not against a surface, the turbulence is expected to be reduced. Therefore, an arbitrary reduction of 90% was imposed on the liquid mass transfer coefficient. Even with the 90% reduction, the loss of VOCs from the weir was predicted to account for 20 to 40 percent of the clarifier losses. The value of the partition coefficient can be estimated from Henry's constant.

Surface Aeration

The model for VOC release resulting from surface aeration should account for the following factors:

- Different rates of VOC release in the agitated zone and the relatively still liquid zones.
- Biological decay
- Predictive functionalities (power input, number of agitators, geometry) which influence emissions and are potentially subject to regulatory control.
- Adsorption rates of VOCs on primary and secondary sludges.

The surface aeration vessel is assumed to be well mixed and at a uniform concentration. Under these conditions, the biological decay rate is expected to be a constant as is the rate of VOC loss into the atmosphere for a given influent concentration. This surface aeration model applies to continuous flow systems and does not apply to batch processing systems. In batch systems, some of the VOCs are lost in the first few hours and the rate of emissions decreases until the next batch charge. For batch operations where the biomass concentration in the aeration vessel is approximately constant, the rate of biooxidation may still be approximately constant in many cases. The losses of VOCs in such systems can be calculated by numerical integration over time, with the VOC concentration, and thus the driving force for volatilization decreasing between charges.

The biological rate is assumed to be a constant for the continuous flow system, but the rate is a function of the operational variables (parameters)

$$B_i = B(X_i, X_{O_2}, M, T) \tag{32}$$

where

B_i = rate of removal of component i (sec^{-1})

X_{O_2} = mole fraction dissolved oxygen

X_i = mole fraction component i

M = biomass concentration (g/L)

T = temperature.

In addition, the biological decomposition process can generate VOCs by forming intermediate decomposition products, with rate constant G_i (sec^{-1}).

$$G_i = G(X_i, X_{O_2}, M, T) \ . \tag{33}$$

In general, these products are oxygenates and may be photochemically active and, therefore, of potential regulatory concern.

The material balance for component i can be written as the sum of the amount flowing out of the system, the amount adsorbed on the sludge, the amount lost to the atmosphere, and the amount destroyed biologically; these are equal to the amount of a VOC entering the aeration vessel.

$$QX_{i,in} = QX_{i,out} + K_{OL}X_{i,out}A/(100\ \rho_m') + B_iVX_{i,out} + Sk_sX_{i,out} \tag{34}$$

where

S = sludge removal rate, m^3/sec

k_s = sludge partition coefficient, (gVOC/cc wet sludge)(gVOC/cc effluent).

Therefore,

$$X_{i,out} = QX_{i,in}/[Q + K_{OL}A/(100\ \rho'_m) + B_iV + Sk_s] \tag{35}$$

The sludge partition coefficient can be experimentally determined, or estimated using Equation (27). The fraction of the VOC entering the aeration vessel which is lost to the air, F, is given by

$$F = K_{OL}X_{i,out}A/(100\ \rho'_m QX_{i,in}) \tag{36}$$

For the generation of VOCs from biotreatment (intermediate decomposition products), the total VOC lost can be estimated from the sum of individual VOCs lost. The concentration of specific VOCs in the system can be obtained by a material balance.

It is assumed that the concentration of the bioproduct entering the system is negligible or that the rate of generation of bioproduct exceeds the amount entering the system by a substantial amount. The component balance for bioproducts can then be written as:

$$VG_i = QX_{i,out} + 0.01\ K_{OL}X_{i,out}A/\rho'_m + B_iVX_{i,out} + Sk_sX_{i,out} \tag{37}$$

where

G_i = rate of generation of intermediate, $gmole/m^3$-sec.

The effluent concentration of the intermediate is then given by

$$X_{i,out} = VG_i/(Q + 0.01\ K_{OL,i}A/\rho'_m + B_iV + Sk_s) \tag{38}$$

The ratio of the amount emitted to the atmosphere to the amount discharged from the process in the liquid effluent can be obtained from the ratio of the rate of air emissions to the rate of discharge.

$$\text{Ratio} = \frac{K_{OL,i}A}{100\ \rho'_m Q} \tag{39}$$

Note that an evaluation of $K_{OL,i}A$ and the effluent concentration would permit an estimation of air emissions, independent of bio-oxidation rates and byproduct generation rates.

Freeman (1982a) predicted that a minimum rate of emissions would occur whenever just enough aeration was present to support the biological activity of the waste treatment process. Materials such as vinyl chloride that are resistant to biological decay are more rapidly lost at higher agitation rates. It should be noted that these results are dependent on the rate constants of the respective processes, as well as the models used. The Gerber kinetic model used in Freeman (1982a) assumes first order kinetic behavior with respect to the oxygen content and may not apply for some systems.

The overall mass transfer coefficient can be estimated by the equations of Thibodeaux (1978) (Appendix A, Equation B) and Reinhart (1977) (Appendix A, Equation J); for the regions outside the agitated zone, the correlations of Owens, et al. (1964) could be used. These equations are discussed in Section 4 and summarized in Appendix A.

Secondary Clarifier

The rate of emissions from a secondary clarifier is estimated in a similar manner to that of a primary clarifier. There will be some biological activity in the secondary clarifier but since the aeration is limited and the biomass settles, the biodegradation rate is much lower than that in the aeration basin and can be neglected. The model is, therefore, identical to that of the primary clarifier.

Trickling Filter

In a trickling filter, water is sprayed over a bed of solids. There are potential emissions as the water droplets fall to the bed. Based upon the model of Calderbank (see equation 24) approximately 12% of the benzene in a dilute solution would be lost as a 0.5 cm droplet of water fell 53 cm. As an example, for a typical trickling filter fall distance of 23 cm (9 inches), the loss of benzene would be approximately 6%.

Most of the VOC emissions would be expected to come from mass transfer on the packing of the trickling filter. With an average packing diameter of 7 cm (2 3/4 inch) the surface area of a randomly packed (porosity 50%) bed would equal 1.7 cm^2/cm^3. A typical VOC liquid phase mass transfer coefficient, $K'_{OL}a$, for a wetted packing is 0.5 to 1.6 min^{-1} (Stallings, et al. 1985). The $K'_{OL}a$ for a specific system is measured for actual operating conditions, since $K'_{OL}a$ is a function of the liquid and gas flow rates, as well as the system geometry.

The mole fraction of a VOC remaining in the treated wastewater, $X_{i,out}$, is estimated by the following equation:

$$\rho_m' Q_L X_{i,in} = \rho_m' Q_L X_{i,out} + K_{OL}' aV(X_i - X_i^*) \rho_m' \tag{40}$$

where X_i^* is the equilibrium concentration of VOC_i in the liquid phase at the air water interface, and Q_L denotes the wastewater flow rate.

Assuming $X_i^* = 0$ (liquid transfer rate controlled) and the model plant parameters of

$V = 4\ (10^3)\ m^3$

$K_{OL}'a = 1.0\ min^{-1}$

$Q_L = 17\ m^3/min$,

the fraction of VOCs emitted by mass transfer from the packing of the trickling filter is:

$$F = 1\text{-}\exp \frac{-\ (1\ min^{-1})\ (4)(10^3)\ m^3}{17\ m^3/min} \cong 1\ . \tag{41}$$

This indicates that at high air flow rates the filter would strip most of the VOCs out of the water if the biological decay rate is sufficiently slow.

No verified models are available for combining the rate of stripping with biological decay; however, the following equations illustrate a potential approach. The rate of loss of VOCs in a trickling filter may be described with the same equations as used for stripping columns (Truong and Blackburn, 1984),

$$\frac{dX}{dt} = K_{OL}'a(X - X^*) \tag{42}$$

where

$K_{OL}'a$ = the liquid based rate constant, min^{-1}

X = the mole fraction of VOC in wastewater

* = the hypothetical mole fraction at equilibrium with the gas.

The solution assuming $X^* = 0$ (liquid transfer rate controlled) is:

$$\ln \frac{x}{X_o} = -K_{OL}'at \tag{43}$$

If biological decay is significant, Equation 36 can be modified to estimate the emissions loss

$$dX = K'_{OL}aXdt + XBdt \ . \qquad (44)$$

The solution is:

$$X = X_o \exp\,[-(K'_{OL}a + B)t] \qquad (45)$$

Where the biological decay rate constant is independent of the VOC concentration:

$$\ln \frac{B' + K'_{OL}a\ X}{B' + K'_{OL}a\ X_o} = K'_{OL}at \qquad (46)$$

where B´ is the biological rate constant based on mole-fraction.

The fraction lost to the atmosphere assuming a constant biological decay rate constant would be estimated by the following relationship:

$$F = \frac{K'_{OL}a}{(K'_{OL}a + B')} \{1-\exp[-(K'_{OL}a + B')t]\} \qquad (47)$$

The other limiting case occurs where the gas is approximately at equilibrium with the wastewater. From a mass balance,

$$(X_{in} - X_o)Q_L\rho'_m(10^6) = Q_g\rho'_{mg}KX_{in} \qquad (48)$$

where Q_g is the gas flow rate, m^3/sec, and ρ'_{mg} is the gas density, g/cm^3 and K is the gas/water partition coefficient based on mole fraction. Solving the preceeding equation for the fraction lost to the atmosphere,

$$F = Q_g\rho'_{mg}K/(10^6Q_L\rho'_m) \qquad (49)$$

Subsurface Aeration

In the process of subsurface aeration, air is bubbled under the surface of an activated sludge basin and the bubbles rise to the surface. It is assumed that the bubbles have attained an equilibrium concentration based upon the thermodynamic partitioning of the VOCs into the gas phase. VOCs can have several potential fates:

- Pass through the system (water or sludge)
- Volatilize into the bubbles
- Volatilize at the surface
- Biodegrade

The mass transfer of compound i to the atmosphere, flux_i includes both a surface diffusion term and a bubble equilibrium term:

$$\text{flux}_i \ (\text{gmol/sec-cm}^2) = K_{OL}X_i + \rho'_{mg}KX_iQ_g/A \qquad (50)$$

The fraction lost to the atmosphere may be calculated as the sum of the fraction lost to bubbles and the fraction lost from surface volatilization.

$$F = \frac{(0.01\ K_{OL}A + \rho'_{mg}\ KQ_g\ 10^6)}{(Q_L\rho'_m + 0.01\ K_{OL}A + 10^6\ \rho'_{mg}\ KQ_g + B_iV\rho'_m)} \qquad (51)$$

The surface mass transfer coefficients, k_L and k_g in subsurface aeration systems are estimated by methods similar to that of surface aeration systems.

Equalization

Equalization takes place in large mixing tanks and insures that concentrated surges of material do not shock the biooxidation systems. It is assumed that the equalization tank is well mixed. The model of MacKay (1983) is used to predict the liquid and gas phase mass transfer coefficients. The rate of biological decay and adsorption in the equalization basin is assumed to be negligible.

Storage Tanks

The atmospheric emissions from storage tanks are estimated by mass transfer coefficients, and the average emissions were estimated using an exponential decay model given in Appendix A (equations K and L). To convert the mass transfer coefficients to emission models for the cases of mixing and no mixing, assumptions were developed for the size and residence time.

The emissions from storage tanks (Equation D of Appendix A) are assumed to be working losses, with turnover factor of 1.0 (dimensionless). The working losses predicted by this equation are substantially greater than the emissions from a storage tank with a floating roof (which can be considered an emission control device) or from a storage tank with only breathing losses. In these situations, Equation D does not properly model the emissions in cases where wind is permitted to blow through the storage tanks because these systems can emit VOCs even when the tank is not being filled. In these situations, Equation D could seriously underestimate the emissions. Also, for the special situation in which a waste liquid was handled more often than assumed, more VOCs could be emitted than predicted by the model. Equation D should be used to estimate the emissions from each tank.

For open tanks with mixing (Equation K, Appendix A), the emissions can be estimated from an equation that accounts for the depletion of volatiles with time as the open tank is agitated. The overall mass transfer coefficient is calculated much like the zone of agitation in agitated impoundments. In a similar fashion, the emissions from open tanks with no mixing (Equation L, Appendix A) are estimated by using an overall mass transfer coefficient obtained from the conditions of the surface impoundment.

Dissolved Air Flotation

In a dissolved air flotation unit, air bubbles pass through the wastewater and volatile components are lost to the atmosphere through these bubbles. The partition coefficients are used to estimate the concentration of the bubbles. The mass transfer coefficients are obtained from McKay (1983) (Appendix A, Equation N) for the gas phase and Churchill (1962) for the liquid. The air emissions from the bubbles are assumed to be added to the emissions from the surface.

Spray Ponds

Spray ponds are simply shallow ponds, typically three feet deep, with a system of pumps and nozzles to spray wastewater into the air. Most of the VOC emissions will result from mass transfer from the sprayed wastewater droplets to the air. The actual emissions will depend upon the flow rate of the pumps and the type of spray nozzle employed. These operating parameters will determine the droplet velocity, size distribution, and projection (i.e., air residence time).

If the droplet size and velocity are known, then the equation of Treybal (1968) (see Equation 16) can be used to estimate the overall mass transfer coeffcient. The rate of droplet fall can be estimated by equations from McCabe and Smith (1967). When the droplet size and falling distance is such that the droplet evaporates to dryness, it can be assumed that all of its contents, volatiles, and nonvolatiles, may be released into the atmosphere as either vapors or aerosols. Consequently, spray ponds can be a major source of VOC emissions.

The pond may contain biologically active material and could be modeled in a manner similar to the surface aeration process previously discussed. The agitated zone would be the surface area in which the wastewater droplets return to the pond. The power input term in Equation B, Appendix A (Thibodeaux, 1978) would be estimated from the kinetic energy of the falling liquid droplets. Such a correlation between droplet kinetic energy and agitator power requirements is not readily available, but it may be developed to apply Thibodeaux's equation for such an aerated system. Nonetheless, the mass transfer coefficients of the droplets are much greater than those for either the agitated or the nonagitated surfaces. Consequently, droplet evaporation accounts for almost all of the VOC emissions that occur from a spray pond.

Cooling Towers

A cooling tower is a large column in which water is evaporatively cooled. The water forms a thin film on the walls and packing of the tower which can greatly enhance mass transfer due to the high surface area. Typically, baffles are employed to enhance liquid mixing and heat transfer. If the cooling water contains VOCs (e.g. recycled wastewater or contaminated groundwater), emissions can be significant for the following two reasons: (1) a large mass transfer coefficient exists due to the short diffusional pathlength, and (2) the recirculation of the cooling water from the tower, to the process, and back to the tower increases the effectiveness of the air-stripping process.

Mass transfer coefficients for falling films can be estimated by equations given by Treybal (1968) (refer to Equation 16). The model employed would be adapted to account for the recirculation rate and the number of baffles for the specific cooling tower geometry. In general, however, cooling water does not contain large amounts of VOCs. Thus, air stripping of VOCs from cooling towers, though effective, is not typically significant.

A COMPARISON OF THE PREDICTIONS OF THE MATHEMATICAL MODELS WITH REPORTED VOC LOSSES FROM AERATION PROCESSES

This section provides examples of the use of the mathematical models described in this document to predict the VOC losses from aeration systems for which VOC emission data are available. A description is provided of (1) how the input parameters were specified, (2) the results of the calculations, and (3) the success of the models at predicting VOC losses.

Parameter Specification

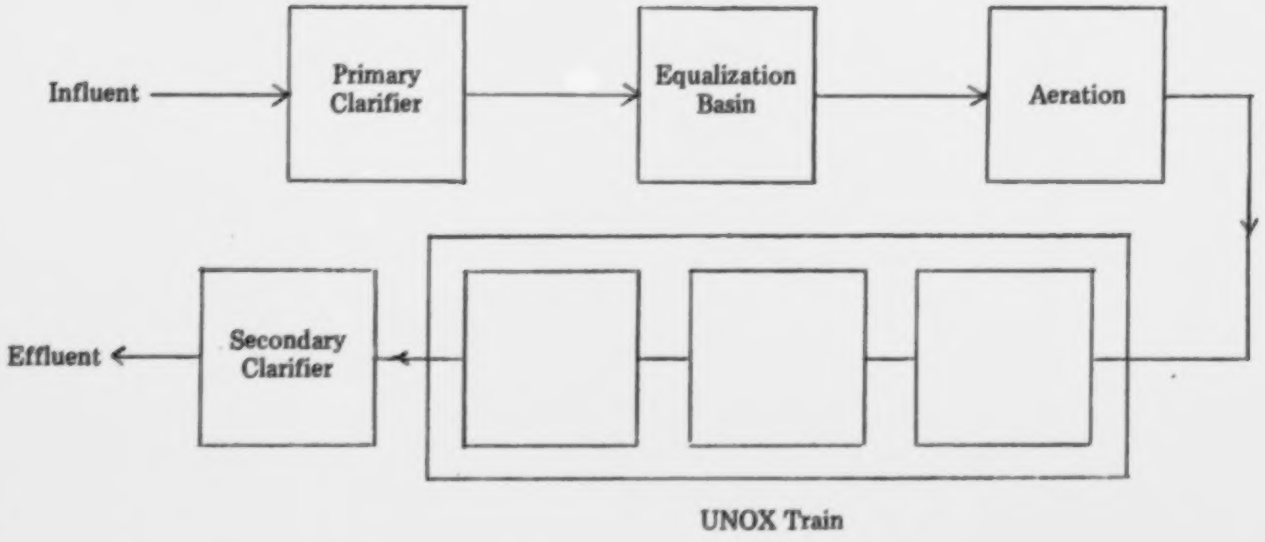
The model provides a specification of the fractional loss of VOCs to the air, to biological decay, and to the outflow of the process unit. This reliance on unit processes provides flexibility; different process configurations can be simulated with the standard default settings, and the input concentrations are not needed to calculate fractional losses to the atmosphere. The unit model approach does have disadvantages; the user must select which unit operations are of concern and perform some simple calculations to obtain air emission rates. For example, if 20 percent of the VOC of interest is lost in the primary clarifier and 30 percent is lost in the following equalization basin, the overall loss would be the sum of 20 percent and (1-.2) (.3)x100 or 44 percent. If the flow of benzene into this system is 30 g/sec, then the air emissions would be calculated as 30 x 0.44 or 13.2 g/sec. In a detailed estimation of national emissions, these site specific calcuations could be performed using the model, with a few changes in the program.

An example of model plant parameters which must be specified are identified in Table 24. The parameters shown are obtained from actual plant data or from model plants. The component properties are selected from an internal data file. The user can scan these component data files and select the components of interest (e.g., benzene, trichloroethane, tetralin). The model was applied to an industrial waste system (Union Carbide) described by Alsop, et al. (1984). A simplified schematic is given in Figure 5. No independent biokinetic data were available for this study and default values of negligibly slow biorates were assumed. The process parameters for this plant were used as default values for the other plants described in this report.

Table 25 presents the physical properties input to the mathematical models. The partition coefficient was estimated from the ratio of the vapor pressure to the solubility. These data are compared to experimentally obtained partition coefficients in Table 26. In some cases, the theoretical values vary significantly from experimental data. The specification of partition coefficient is, however, an input to the model which may be specified based on the best available information. Theoretical data were used in this report.

TABLE 24. MODEL INPUT DATA FOR UNION CARBIDE PLANT
(Alsop, et al. 1984)

Temperature (deg C)	25
Air Velocity (cm/s)	200
Concentration of Benzene (mole fract)	.001
Concentration of Naphthalene (mole fract)	.005
Concentration of Ethylbenzene (mole fract)	.001
Concentration of Methyl cellosolve (mole fract)	.0002
Concentration of Tetralin (mole fract)	.0001
Biorate of Benzene (hours)	400
Biorate of Naphthalene (hours)	400
Biorate of Ethylbenzene (hours)	400
Biorate of Methyl cellosolve (hours)	800
Biorate of Tetralin (hours)	200
Waste flow rate (m^3/sec)	.07
Area of pretreatment basin (m^2)	50
Depth of pretreatment basin (m)	3
Diameter of clarifier (m)	19.4
Depth of clarifier (m)	2.4
Number of clarifiers	1
Length of aeration basin (m)	170
Width of aeration basin (m)	170
Depth of aeration basin (m)	3.6
Area of agitators, each (m^2)	96
Number of agitators	30
Power of agitation, each (hp)	75
Impeller diameter (cm)	30
Impeller rotation (rpm)	2000
Number of secondary clarifiers	1
Diameter of secondary clarifier (m)	37
Depth of secondary clarifier (m)	3
Area of equalization basin (m^2)	5185
Depth of equalization basin (m^2)	3
Air flow in DAF (pretreat) (sm^3/s)	0
Flow of submerged air (m^3/sec)	.4
Power of sub-agitation, each (hp)	50
Length of sub-aeration basin (m)	33.5
Width of sub-aeration basin (m)	8.4
Depth of sub-aeration basin (m)	8.5
Area of sub-agitators (each) (m^2)	70.1
Number of sub-units in series	3
Impeller rotation (rpm)	70
Impeller diameter (cm)	243
Weir height (cm)	30
Weir flow thickness (cm)	1
Enter {1} for covered sub-agitators	1


Influent
Primary Clarifier
Equalization Basin
Aeration
Effluent
Secondary Clarifier
UNOX Train

Source: Alsop et al., 1984

Figure 5. Flow scheme for Union Carbide plant.

TABLE 25. PHYSICAL PROPERTY DATA USED IN MATHEMATICAL MODEL

Compound	Water diffusivity cm^2/sec	Air diffusivity cm^2/sec	Molecular weight	Partition coefficient
BENZENE	0.000010	0.088	78	305
TOLUENE	0.000009	0.067	92	366
XYLENE	0.000008	0.063	106	300
PHENOL	0.000009	0.082	94	0
METHANOL	0.000016	0.149	32	0
111 TCE	0.000009	0.064	133	273
ACETONE	0.000011	0.103	58	0
BUTANOL	0.000010	0.079	74	1
ETHANOL	0.000013	0.112	46	0
ACRYLONITRILE	0.000012	0.102	41	4
METHYL CHLORIDE	0.000014	0.114	50	2044
METHYLENE CHLORIDE	0.000010	0.100	99	177
VINYL CHLORIDE	0.000012	0.093	63	30000
CARBON TETRACHLORIDE	0.000010	0.063	154	1679
OXYGEN	0.000025	0.178	32	4000
ETHYL BENZENE	0.000008	0.070	106	271
2 ETHYL HEXANOL	0.000007	0.090	130	1
NAPHTHALENE	0.000008	0.059	128	65
TETRALIN	0.000008	0.070	132	600
DICHLOROETHANE	0.000010	0.080	99	61
METHYL CELLOSOLVE	0.000010	0.080	76	0
CELLOSOLVE	0.000010	0.080	90	0
METHYL CELLOSOLVE ACETATE	0.000008	0.070	118	0
CELLOSOLVE ACETATE	0.000008	0.070	132	0
1-OCTENE	0.000008	0.070	112	53
CHLOROBENZENE	0.000009	0.090	113	224
CHLOROFORM	0.000007	0.080	120	186
112 TRICHLOROETHANE	0.000008	0.070	133	47
TETRACHLOROETHANE	0.000008	0.060	168	24
TETRACHLOROETHYLENE	0.000008	0.060	166	1547
TRICHLOROETHYLENE	0.000009	0.060	131	650
DICHLOROETHYLENE	0.000010	0.075	97	856

TABLE 26. A COMPARISON OF MEASURED AND THEORETICAL PARTITION COEFFICIENTS (Petrasek et al., 1983)

Component	Partition Coefficient (Y/X)	
	Experimental[a]	Model[b]
Dichloroethene	150	856
Chloroform	164	186
Carbon tetrachloride	1138	1679
1,1,2 Trichloroethane	16.7	47
Benzene	795	300
1,1,1 Trichloroethane	2409	273
Chlorobenzene	81	224
Tetrachloroethane	54	24
Toluene	792	329
Ethyl Benzene	859	271

[a] Obtained from the ratio of the concentration in the off-gas to the exit liquid concentration.

[b] Obtained from the ratio of the vapor pressure to the solubility in water.

Results of Calculations

Table 27 presents the comparison of the calculations of the model with the reported VOC losses for benzene, ethylbenzene, toluene, dichloroethane, naphthalene, and tetralin. The losses from the clarifier were reported as the sum of the loss from the surface and the loss from the overflow. The UNOX losses are based upon a closed system.

An investigation of VOC losses in the Water Environmental Research Laboratory (WERL) pilot facility (Petrasek, 1981) is compared to the results of the model. A schematic of the WERL pilot plant is shown in Figure 6. The results of this comparison are presented in Table 28. The parameters specified in the model are presented in Table 29. Many of the critical parameters were available from the report.

Additional WERL data were published by Petrasek (1983). Table 30 presents a comparison of the loss of VOCs from the WERL pilot facility based upon the measured VOC emission rates and the model rates. Two numbers are presented in the experimental column, representing the results from the two parallel treatment units. Analyses of the off-gas from the aeration process indicated that there was an average VOC loss of 43 percent due to volatilization in the aeration basin. Table 31 presents the input parameters for the models.

Tables 32 and 33 present the comparisons of the predicted and reported VOC losses from the American Cyanamid Willow Island Plant and the parameter assumptions, respectively. In a similar fashion Tables 34 and 35 describe a comparison for the Sisterville Plant, and Tables 36 and 37 describes a comparison for the du Pont Belle Plant (Lassiter, P.E., Memo 1985).

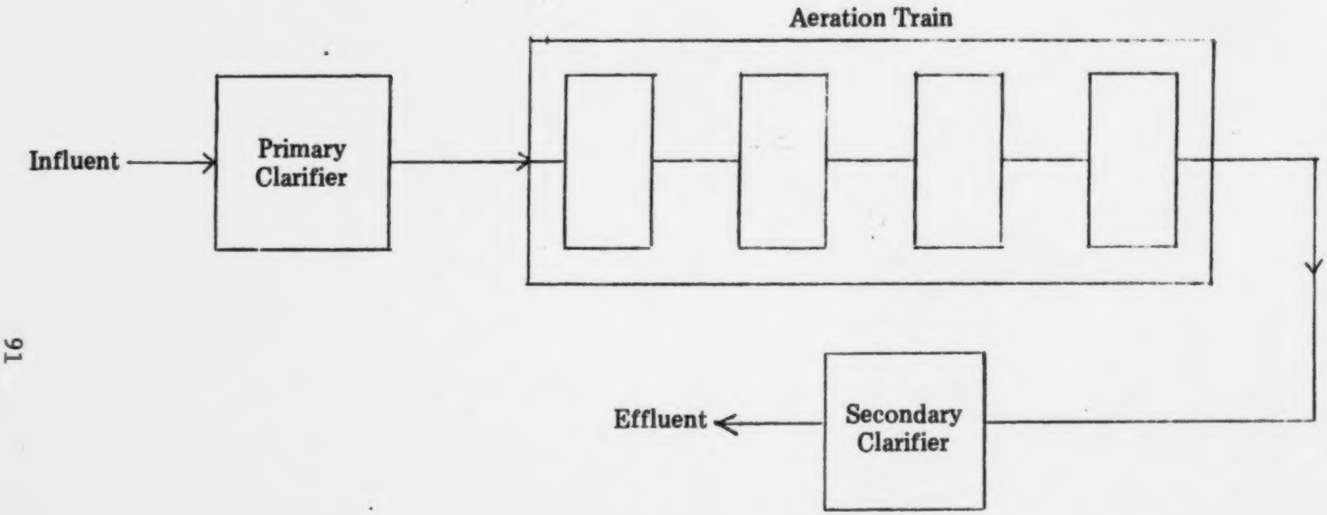
Discussion of the Model Applicability

The rate of loss of volatiles from the Union Carbide Plant (Alsop, et al. 1984) as predicted by the mathematical models agreed well with measured results, with the exception of the UNOX biological treatment unit. The rate of removal in the UNOX system was overpredicted by the model, particularly in the case of tetralin. It is unknown whether analytical procedures or nonlinear K values for tetralin were responsible for the variation. Though the loss in the aeration basin was overpredicted by the model for tetralin and naphthalene (89% was the observed loss in both cases), the absolute errors were still only

TABLE 27. A COMPARISON OF THE EXPERIMENTAL LOSS OF VOLATILES FROM THE UNION CARBIDE PLANT FIELD TEST TO THE PREDICTED LOSS FROM MATHEMATICAL MODELS (Alsop, et al., 1984)

Unit/volatile	Fractional loss (experimental)	Fractional loss to air (predicted)
Clarifier surface		
Benzene		.16
Ethyl benzene		.15
Toluene		.15
Dichloroethane		.13
Naphthalene		.12
Tetralin		.15
Clarifier overflow		
Benzene		.01
Ethyl benzene		.01
Toluene		.01
Dichloroethane		.01
Naphthalene		.006
Tetralin		.01
Total Clarifier		
Benzene	.058	.17
Ethyl benzene	.103	.16
Toluene	.13	.16
Dichloroethane	.143	.14
Naphthalene	.045	.116
Tetralin	.225	.16
Equalization basin		
Benzene	.391	.31
Ethyl benzene	.35	.29
Toluene	.281	.29
Dichloroethane	.389	.31
Naphthalene	.269	.27
Tetralin	.115	.29
Aeration basin		
Benzene	.9984	.998*
Ethyl benzene	.993	.997*
Toluene	.993	.998*
Dichloroethane	.987	.994*
Naphthalene	.892	.994*
Tetralin	.905	.998*
UNOX		
Benzene	.26	.58*
Ethyl benzene	.44	.55*
Toluene	.19	.62*
Dichloroethane	-.08	.23*
Naphthalene	.31	.26*
Tetralin	.05	.73*

*Includes biological loss (approximately 0.01).


Aeration Train
Influent
Primary Clarifier
Secondary Clarifier
Effluent

Based on Petrasek, 1981

Figure 6. WERL pilot plant flow scheme.

TABLE 28. A COMPARISON OF THE EXPERIMENTAL LOSS OF VOLATILES FROM A MERL PILOT STUDY TO THE PREDICTED LOSS FROM MATHEMATICAL MODELS (Petrasek, 1981).

Unit/Volatile	Fractional loss (experimental)	Fractional loss (predicted)
Clarifier surface		
Methylene chloride		.065
Benzene		.063
Trichloroethane		.063
Dichloroethene		.067
Carbon tetrachloride		.066
Clarifier overflow		
Methylene chloride		.005
Benzene		.005
Trichloroethane		.005
Dichloroethene		.005
Carbon tetrachloride		.005
Total clarifier		
Methylene chloride	.26	.070
Benzene	.32	.068
Trichloroethane	.85	.068
Dichloroethene	.51	.072
Carbon tetrachloride	.18	.071
Aeration basin		
Methylene chloride	.84	.77
Benzene	.88	.85
Trichloroethane	-.12	.84
Dichloroethene	.95	.94
Carbon tetrachloride	.91	.97

TABLE 29. MODEL INPUT DATA FOR WERL PILOT PLANT STUDY (Petrasek, 1981)

Temperature (deg C)	25
Air Velocity (cm/s)	300
Concentration of Benzene (mole fract)	.001
Concentration of Methylene chloride (mole fract)	.005
Concentration of 1,1,1-TCE (mole fract)	.001
Concentration of Methyl cellosolve (mole fract)	.0002
Concentration of Carbon tetrachloride (mole fract)	.0001
Biorate of Benzene (hours)	200
Biorate of Methylene chloride (hours)	200
Biorate of 1,1,1-TCE (hours)	200
Biorate of Methyl cellosolve (hours)	200
Biorate of Carbon tetrachloride (hours)	200
Waste flow rate (m^3/sec)	.0022
Diameter of clarifier (m)	3
Depth of clarifier (m)	3.6
Number of clarifiers	1
Number of secondary clarifiers	1
Diameter of secondary clarifier (m)	3.6
Depth of secondary clarifier (m)	3.6
Flow of submerged air (m^3/sec)	.057
Power of sub-agitation, each (hp)	10
Length of sub-aeration basin (m)	3
Width of sub-aeration basin (m)	1.35
Depth of sub-aeration basin (m)	3.6
Area of sub-agitators (each) (m^2)	4
Number of sub-units in series	4
Impeller rotation (rpm)	100
Impeller diameter (cm)	200
Weir height (cm)	9
Thickness of weir flow (cm)	1

TABLE 30. A COMPARISON OF THE EXPERIMENTAL AND PREDICTED LOSS OF VOLATILES FROM A WERL PILOT FACILITY (Petrasek et al., 1983)

	Loss of VOC (%)			
	Clarifier		Subaeration	Total
	Experimental	Predicted	Experimental	predicted[a]
Methyene chloride	27,25	7.0	88.7,99.5	77.4
Dichloroethane	65,57	7.2	94.5,99.4	94.3
Chloroform	33,--	5.6	94.4,97.6	78.3
Carbon tetrachloride	47,47	7.1	94.0,99.3	97.0
Trichloroethylene	31,36	6.7	93,97.8	92.6
Benzene	--,16	6.8	88,99.6	85.5
Trichloroethane	48,27	6.8	97,99.7	84.1
Toluene	29,22	6.3	93.5,99.6	87.6
Ethyl Benzene	70,16	6.3	97,99.7	84.0
Tetrachloroethylene	88	6.3	93	96.7

[a] air emissions (lost to bubbles only) plus biological decomposition.

TABLE 31. MODEL INPUT DATA FOR WERL PILOT STUDY
(Petrasek, 1983)

Temperature (deg C)	25
Air Velocity (cm/s)	300
Concentration of Benzene (mole fract)	.001
Concentration of Methylene chloride (mole fract)	.005
Concentration of 1,1,1-TCE (mole fract)	.001
Concentration of Methyl cellosolve (mole fract)	.0002
Concentration of Carbon tetrachloride (mole fract)	.0001
Biorate of Benzene (hours)	200
Biorate of Methylene chloride (hours)	200
Biorate of 1,1,1-TCE (hours)	200
Biorate of Methyl cellosolve (hours)	200
Biorate of Carbon tetrachloride (hours)	200
Waste flow rate (m^3/sec)	.0022
Diameter of clarifier (m)	3
Depth of clarifier (m)	3.6
Number of clarifiers	1
Number of secondary clarifiers	1
Diameter of secondary clarifier (m)	3.6
Depth of secondary clarifier (m)	3.6
Flow of submerged air (m^3/sec)	.057
Power of sub-agitation, each (hp)	10
Length of sub-aeration basin (m)	1.35
Width of sub-aeration basin (m)	3
Depth of sub-aeration basin (m)	3.6
Area of sub-agitators (each) (m^2)	100
Number of sub-units in series	4
Impeller rotation (rpm)	100
Impeller diameter (cm)	200
Weir height (cm)	9
Thickness of weir flow (cm)	1

TABLE 32. A COMPARISON OF THE REPORTED FRACTIONAL LOSS OF COMPONENTS FROM PRIMARY WASTEWATER TREATMENT AND THE PREDICTED LOSSES, WILLOW ISLAND PLANT (Lassiter, P.E., Memo, 1985), American Cyanamid

Component	Fractional loss of VOC Reported	 Predicted
Ethyl Cellusolve	0.071	0.0023
Methanol	0.41	0.0152
1-octene	0.13	0.259

TABLE 33. MODEL INPUT DATA FOR WILLOW ISLAND WASTEWATER STUDY (Lassiter, P.E., Memo, 1985)

Temperature (deg C)	25
Air Velocity (cm/s)	200
Concentration of Methanol (mole fract)	.001
Concentration of Ethyl cellosolve (mole fract)	.005
Concentration of 1-octene (mole fract)	.001
Biorate of Methanol (hours)	500
Biorate of Ethyl cellosolve (hours)	500
Biorate of 1-octene (hours)	500
Waste flow rate (m^3/sec)	.127
Area of pretreatment basin (m^2)	3
Depth of pretreatment basin (m)	3
Diameter of clarifier (m)	19.4
Depth of clarifier (m)	2.4
Number of clarifiers	1
Weir distance (cm)	30
Thickness of weir flow (cm)	1

TABLE 34. A COMPARISON OF THE ESTIMATED FRACTIONAL VOC LOSS AND THE PREDICTED VOC LOSS FOR THE SISTERVILLE PLANT
(Lassiter, P.E., Memo, 1985)

Compound	Fractional Loss	
	Estimated+	Predicted++
Ethanol	.005	0.0008
Methanol	.005	0.0016
Toluene	.128	0.157

+ Plant emissions
++ Primary treatment, no equalization

TABLE 35. MODEL INPUT DATA FOR SISTERVILLE WASTEWATER STUDY
(Lassiter, P.E., Memo, 1985)

Temperature (deg C)	25
Air Velocity (cm/s)	200
Concentration of Ethanol (mole fract)	.001
Concentration of Methanol (mole fract)	.005
Concentration of Toluene (mole fract)	.001
Biorate of Ethanol (hours)	400
Biorate of Methanol (hours)	400
Biorate of Toluene (hours)	400
Waste flow rate (m^3/sec)	.08
Diameter of clarifier (m)	19.4
Depth of clarifier (m)	2.4
Number of clarifiers	1
Weir height (cm)	30
Thickness of weir flow (cm)	1

TABLE 36. A COMPARISON OF THE ESTIMATED AND PREDICTED FRACTIONAL LOSS OF VOCs TO THE AIR FROM PRIMARY AND SECONDARY TREATMENT AT THE DU PONT BELLE PLANT (Lassiter, P.E., Memo 1985)

Component	Primary+		Secondary++	
	Reported	Predicted	Reported	Predicted
Methanol	0.015	0.024	0.000001	0.0005
Acetone	0.008	0.035	0.0015	0.0009
Chloroform	0.62	0.375	0.0062	0.393
Butanol	0.0007	0.120	NR	0.0045

+ Pretreatment, clarifier, equilization

NR = not reported

++ aeration, submerged and covered

TABLE 37. MODEL INPUT DATA FOR DUPONT BELLE WASTEWATER STUDY
(Lassiter, P.E., Memo, 1985)

Temperature (deg C)	25
Air Velocity (cm/s)	200
Concentration of Methanol (mole fract)	.001
Concentration of Butanol (mole fract)	.005
Concentration of Acetone (mole fract)	.001
Concentration of Chloroform (mole fract)	.0002
Biorate of Methanol (hours)	400
Biorate of Butanol (hours)	400
Biorate of Acetone (hours)	400
Biorate of Chloroform (hours)	400
Waste flow rate (m^3/sec)	.08
Area of pretreatment basin (m^2)	50
Depth of pretreatment basin (m)	3
Diameter of clarifier (m)	19.4
Depth of clarifier (m)	2.4
Number of clarifiers	1
Number of secondary clarifiers	1
Diameter of secondary clarifier (m)	37
Depth of secondary clarifier (m)	3
Area of equalization basin (m^2)	5185
Depth of equalization basin (m^2)	3
Air flow in DAF (pretreat) (sm^3/s)	0
Flow of submerged air (m^3/sec)	.4
Power of sub-agitation, each (hp)	50
Length of sub-aeration basin (m)	33.5
Width of sub-aeration basin (m)	8.399999
Depth of sub-aeration basin (m)	8.5
Area of sub-agitators (each) (m^2)	70
Number of sub-units in series	3
Weir height (cm)	30
Thickness of weir flow (cm)	1

5-10%. Therefore, it may be concluded that the models were successful in simulating the field conditions for the plant, and that most of the VOCs were lost to the atmosphere.

In an EPA pilot investigation (Petrasek, 1981) a number of VOCs were processed in a clarifier followed by an aerated biological oxidation unit. Enough data were provided to specify the input parameters of the model. Although the treatment plant was not directly exposed to the atmosphere, air was circulated and the mass transfer is considered to be liquid phase controlled. For both the clarifier and the aerator, the model predicted VOC losses in close agreement with the pilot data. The model predicted that most of the VOCs were lost to the circulating air. While there was good agreement between the predicted and experimental emissions rates for subsurface aeration in more recent work at the WERL Pilot Facility (Petrasek, 1983), the experimental results for the clarifier VOC losses appear anomalously high. However, Petrasek did not discuss this possible discrepency and, therefore, is it not possible to determine whether the modelled or experimental results are in error.

The fractional loss of VOCs to the air was estimated for the du Pont Belle plant (Table 36). The model predictions for methanol, acetone, and chloroform were within a factor of 5 for the primary process, but did not agree with the estimated losses of butanol. The secondary treatment estimations did not agree with model predictions. Not enough information was provided to determine the source of the difference. At the Union Carbide Sisterville plant, the predicted fractional loss was within a factor of 5 of the estimated values. Only primary treatment was assumed; no information was provided about the source characteristics except for the flow rate. The reported values of the VOCs lost from the American Cyanamid Willow Island plant did not agree with the predicted values. No information about the source characteristics (except flow rate) was available.

In the two wastewater treatment units for which source descriptions as well as dependable field measurements were available, the agreement of the model with the reported VOC losses was acceptable (considering sampling and analysis errors) for estimation of emissions. In situations where the source characteristics were not known the prediction of the model was less accurate. The accuracy of the reported values has not been established; no changes in the model are recommended based on these limited data.

SECTION 6

NOMENCLATURE

a	interfacial surface area/bed volume, cm^2/cm^3
A	surface area, cm^2
A_e	effective surface area of a particle, cm^2
C	concentration, $gmol/cm^3$
C_o	concentration at time = 0, $gmol/cm^3$
D	impeller diameter, cm
D_e	effective diameter of nonagitated surface, m
D_{AB}	diffusion coefficient of component A in B, cm^2/sec
D_f	diffusion coefficient in film, cm^2/sec
D_{VOC}	diffusion coefficient of VOC, cm^2/sec
e	emission rate, gmol/sec
F_A	fraction of waste in agitation impoundment from source
F	fraction of VOC lost to the atmosphere
Fr	Froude number
g_{hf}	gas holdup fraction, v_g/v_b
Gi	rate of VOC (component i), generation, $gmol/cm^3$-sec
G_c	gravitational constant
h	liquid height or depth, cm
H	Henry's Law Constant, cm^3-atm/g-mol
J	oxygen transfer rating
K_{fL}	film-liquid partition coefficient
K	partition coefficient, Y/X
k_g	mass transfer coefficient of gas, g-mol/cm^2-sec
k'_g	mass transfer coefficient of gas, cm/sec

k'_L	liquid mass transfer coefficient $k'_L = k_L(MW)/\rho'_m$, cm/sec
k_L	mass transfer coefficient of liquid, gmol/cm^2-sec
k'_{OL}	overall mass transfer coefficient, cm/sec
K_{OL}^{ref}	overall mass transfer coefficient of a tracer, g-mol/cm^2-sec
K_{OL}	overall mass transfer coefficient based on liquid concentrations, g-mol/cm^2-sec
K_2	oxygen reaeration rate constant (base e), s^{-1}
L	characteristic length, cm
MW	molecular weight, g/gmol
MW_{ave}	Average molecular weight of liquid, g/gmol
ρ'_m	molar density, g-mol/cm^3
ρ_p	particle density, g/cm^3
ρ	density, g/cm^3
P_i	vapor pressure of component i, atm
PI	power input to the agitator or aerator, hp or g-cm^2/sec^3
POWR	power of agitators
Po	Power number
P_{ow}	n-octanol/water partition coefficient
q_i	atmospheric emission rate of component i, g/sec
q_T	total atmospheric emissions, g/sec
Q	volumetric flow rate, cm^3/sec
R	gas constant = 82.05 cm^3 atm/g-mol
Re	Reynold's number
Re^*	roughness Reynold's number
Re_p	particle Reynold's number
ST	surface tension, g/sec^2

τ	residence time, sec
t	time, sec
T	temperature, °C or °K
μ	viscosity, g/cm-sec
U^*	correlated wind velocity = $(6.1 + 0.63\ U_{10})^{0.5}\ U_{10}/100$, in/sec
U	wind velocity, cm/sec
U_{10}	wind velocity at 10 m above surface, m/sec
v	velocity, cm/sec
v_t	terminal velocity, cm/sec
V	volume, cm^3
w	rotation speed, rpm
W	mass flow rate, g/sec
X	mole fraction in liquid phase
Y	mole fraction in gas phase
Γ	liquid mass flow rate per unit film width, g/cm-sec
δ	film thickness, cm

Subscripts

g	denotes gas phase
L	denotes liquid phase
b	bubble
p	particle
i	denotes component i
o	denotes initial condition at $t = 0$.

SECTION 7

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Appendix A

Emission Equations

APPENDIX A
EMISSION EQUATIONS

	References
A. LIQUID MASS TRANSFER WITH WIND	
$k_L = 1.3\ (Re^{0.195} - 0.57)(D_{iwater}/D_{benzwater})^{0.67}$	Based on Cohen, Cocchlo, and MacKay (1978)
B. LIQUID MASS TRANSFER WITH AGITATION	
$K_LaV = [J(POWR)\ \alpha\ 10^6\ (1.024)^{T-20}/165.04]\ (D_{iwater}/D_{oxgnwater})^{0.5}$	Thibodeaux (1978)
C. LIQUID MASS TRANSFER WITHOUT AGITATION	
$k_L = 3.12\ (1.024)^{T-20}\ V_o^{0.67}\ (D_{iwater}/D_{oxgnwater})^{0.66}/(h/3)^{0.85}$ T = the temperature, 25 °C V_o = the surface velocity, 0.035 (14.7 ft/sec) natural surface, 0.1 ft/sec outside region of effect of agitation in biological treatment h = the depth of the liquid, ft $D_{oxgnwater}$ = the diffusion coefficient of oxygen in water	Based on Owens, Edwards, and Gibbs (1964)
D. STORAGE TANKS, FIXED ROOF	
$L_w = 0.01089(MW)p(TP)$ TP = tank throughput, gal/day p = pressure (psia) Assumes all emissions are from tank working losses.	AP42, modified (1981)

Continued

References

E. SURFACE IMPOUNDMENTS

q_T (g/sec) = $A(cm^2)K_{oL}(MW)X$

X = mole fraction of the component in the liquid

H = Vapor pressure (torr)/760 * (MW)/solubility (mg/L)

$K_{oL} = (1/k_L + 1/Kk_g)^{-1}$

k_L = from Owens et al. (1964) $K = 10^6$ /MW

K_g = from Thibodeaux and Parker (1974)

F. AERATION

$q_T = A_1 q_1 + A_2 q_2$

$q_i = K_{oL} C_L$

C_L = the concentration in the liquid (g/cm^3)

K_{oL} (agitation) = $(1/k_L = 1/k_g K)^{-1}$

where k_L from Thibodeaux (1978)

k_g from Reinhart (1977)

K_{oL} (nonagitation) = $(1/k_L + 1/k_g K)^{-1}$

where k_L from Owens et al. (1964)

k_g from MacKay and Mutsuga (1973)

Continued

APPENDIX A (Continued)

	References
A_1 = area agitated	
A_2 = area away from agitation	
G. GAS MASS TRANSFER COEFFICIENT	
$k_g = 0.0958\ U^{0.78}\ \rho_{air}/[28.97(Sc)^{0.67}(D_e)^{0.11}]$	MacKay and Matsuga (1973)
where U = wind velocity, m/hr	
D_e = effective diameter of non-agitated surface, m	
ρ = density, lb/ft^3	
H. GAS MASS TRANSFER COEFFICIENT	
$k = 4.03 \cdot 10^{-6}\ U^{.804}\ L^{-.196}\ D_{i\text{-}air}^{.667}$ (Colburn type equation)	Sherwood and Pigford (1952)
I. GAS MASS TRANSFER COEFFICIENT	
$k_g = 9.9\ U\ D_{i\text{-}air}/[10^7(L)^{0.1}]$	Thibodeaux & Parker (1974)
J. GAS MASS TRANSFER COEFFICIENT	
$k_g = 0.00039\ \rho g\ D_{i\text{-}H_2O}\ (Re)^{1.42}(PN)^{0.4}(Sc)^{0.5}/[D^{0.1}(Fr)^{0.21}]$	Reinhardt (1977)
where k_g is given in lb/(ft^2 hr)	

Continued

APPENDIX A (Continued)

References

K. OPEN TANKS WITH MIXING

q_T (g/day) = w (g/day)[1-exp(-K'_{OL} x τ/h)]

q_T = total emissions, g/day

W = mass flowrate, g/day

τ = residence time (seconds)

h = depth, cm

K'_{OL} = the overall mass transfer coefficient obtained from agitated impoundments, zone of agitation (cm/sec)

L. OPEN TANKS WITH NO MIXING

q_T (g/day) = W (g/day)[1 - exp(-K'_{OL} x τ/h)]

q_T = total emissions, g/day

W = mass flowrate, g/day

τ = residence time (seconds)

h = depth, cm

K'_{OL} = the overall mass transfer coefficient obtained from agitated impoundments, zone of agitation (cm/sec)

Continued

APPENDIX A (Continued)

References

M. COOLING TOWERS

For volatile components (vapor pressure > 3 torr), the rate of emissions is the rate of generation times 0.98. For the other components, use the ratio, emission/generation = vapor pressure/3 torr x 0.98.

Assume the drift loss is .2 percent of recirculation rate.

Assume a recycle of 10 times. The drift loss would then be .02 times the rate of waste generation.

Assume that cooling towers would not be used for organic steams (fraction nonwater > .1) or for sludges (fraction solids > .1).

N. GASS MASS TRANSFER COEFFICIENT

k_g (m/sec) = $0.001 + 0.462\ U^*/(Sc)^{0.67}$ MacKay and Yeun (1983)

where $U^* = (6.1 + 0.63\ U_{10})^{0.5}\ U_{10}/100$

Appendix B

Sample Calculations

APPENDIX B: SAMPLE CALCULATIONS

The sample calculations are divided into three sections. The first illustrates the use of each of the gas mass transfer correlations; the second illustrates the use of each of the liquid mass transfer correlations. The third section demonstrates the overall mass transfer coefficient and fractional removal calculations for each of the different process units modeled.

All of the sample calculations are performed for the component benzene in the Union Carbide (Alsop, et al., 1984) plant. The input parameters for the plant are presented in Table 24. The physical constants for benzene are presented in Table 25. Other constants needed for the sample calculations are given below:

Density = ρ_{air} = 1.185×10^{-3} g/cm^3
Viscosity = μ_{air} = 1.78×10^{-4} g/cm-sec^2
Molecular wt. = MW_{air} = 28.8 g/g mol
Density = ρ_{H_2O} = 1.0 g/cm^3
Viscosity = μ_{H_2O} = 1.0×10^{-2} g/cm-sec
Molecular wt. = MW_{H_2O} = 18 g/g mol
Diffusivity = $D_{O_2-H_2O}$ = 2.5×10^{-5} cm^2/sec.

I. GAS PHASE MASS TRANSFER COEFFICIENTS

A. MacKay and Yeun (1983) (Eq. N, Appendix A)

$$kg' \text{ (m/sec)} = 10^{-3} + 0.0462\, U^* \, Sc_g^{-0.67}$$

$$U^* = (6.1 + 0.63\, U_{10})^{0.5} U_{10}/100 \ .$$

U_{10} = air velocity = 200 cm/sec = 2.0 m/sec .

$$U^* = (6.1 + 0.63(2))^{0.5}(2/100) = 0.0542.$$

$$\text{Schmidt No.} = Sc_g = \frac{\mu_{air}}{\rho_{air} D_{i\text{-}air}} \quad \frac{1.78\times10^{-4}}{(1.185\times10^{-3})(0.088)} = 1.707$$

so that $Kg' = 10^{-3} + 0.0462\ (0.0542)(1.707)^{-0.67} = 2.75 \times 10^{-3}$ m/sec

or $Kg = kg'(\rho_g/MW_g) = (2.75 \times 10^{-3} \times \frac{100}{m}\ \text{cm})(1.185 \times 10^{-3}/28.8)$

$Kg = 1.13 \times 10^{-5}$ g-mol/cm^2-sec.

B. Thibodeaux and Parker (1974) (Eq. I, Appendix A)

$Kg(\text{g-mol/cm}^2\text{-sec}) = 9.9 \times 10^{-7}\ U\ D_{i\text{-}air}/L^{0.1}$

Again, U = 200 cm/sec;

L = length of square impoundment or diameter of round impoundment--e.g., for primary clarifier = 1,940 cm.

$Kg = 9.9 \times 10^{-7}\ (200)(0.088)/(1{,}940)^{0.1}$

$Kg = 8.2 \times 10^{-6}$ g-mol/cm^2-sec.

C. MacKay and Matsuga (1973) (Eq. G, Appendix A)

$$Kg(\text{lb-mol/ft}^2\text{-hr}) = 0.0958\ U^{0.78}(\text{m/hr})(Sc)^{-0.67} \times D(\text{m})^{-0.11}\rho_g(\text{lb/ft}^3)/MW_g$$

$U = 200$ cm/sec (3,600 sec/hr) $\frac{1\ \text{m}}{100\ \text{cm}} = 7{,}200$ m/hr

$Sc_g = 1.707$ (previously calculated in I.A.)

$D = 19.4$ m for primary clarifier

$\rho_g = 1.185 \times 10^{-3}$ g/cm^3 x 62.43 lb-cm^3/g-ft^3 = 0.074 lb/ft^3

$MW_g = 28.8$ g/g-mol = 28.8 lb/lb-mol

$Kg = 0.0958(7{,}200)^{0.78}(1.707)^{-0.67}(19.4)^{-0.11}(0.074)/(28.8)$

$= 0.1267$ lb-mol/ft^2-hr

or $Kg\ (\text{g-mol/cm}^2\text{-sec}) = 0.1267\ (1.356 \times 10^{-4}\ \frac{\text{g-mol-ft}^2\text{-hr}}{\text{lb-mol-cm}^2\text{-sec}})$

$Kg = 1.72 \times 10^{-5}$ g-mol/cm^2-sec.

D. Sherwood and Pigford (1952) (Eq. 4, Appendix A)

$$Kg(\text{g-mol/cm}^2\text{-sec}) = 4.03 \times 10^{-6}\ U^{0.804}\ L^{-0.196}\ D_{i\text{-air}}{}^{0.667}$$

Again, modeling the primary clarifier (constants given in I.B. cgs units)

$$Kg = 4.03 \times 10^{-6}\ (200)^{0.804}\ (1940)^{-0.196} (0.088)^{0.667}$$

$$Kg = 1.28 \times 10^{-5}\ \text{g-mol/cm}^2\text{-sec.}$$

E. Reinhart (1977) (Eq. J, Appendix A)

$$Kg(\text{lb/ft}^2\text{-hr}) = 3.9 \times 10^{-4}\ \frac{\rho_g(\text{lb/ft}^3) D_{i\text{-air}}(\text{ft}^3\text{/hr})}{d_{imp(ft)}}$$

$$\times\ Re^{1.42} Fr^{-0.21} Po^{0.4} Sc^{0.5}$$

$$\rho_g = 1.185 \times 10^{-3}\ \text{g/cm}^3 = 0.074\ \text{lb/ft}^3$$

$$D_{i\text{-air}} = 0.088\ \text{cm}^2\text{/sec} = 0.341\ \text{ft}^2\text{/hr}$$

$$\mu_g = 1.78 \times 10^{-4}\ \text{g/cm-sec} = 1.2 \times 10^{-5}\ \text{lb m/ft-sec}$$

For the aeration basin: Power Input (PI) = 75 HP = 41,250 ft-lb/sec

Impeller diameter = d_{imp} = 30 cm = 0.987 ft

Angular velocity = ω = 2,000 rpm = 2,000(2π/60) = 209.4 rad/sec

$$\text{Reynolds No.} = Re = \frac{d_{imp}^2 \omega \rho_g}{\mu_g} = \frac{(0.987)^2(209.4)(0.074)}{(1.2 \times 10^{-5})} = 1.258 \times 10^6$$

$$\text{Froude No.} = d_{imp}\ \omega^2/g_c = (0.987)(209.4)^2/32.17 = 1{,}345$$

$$\text{Power No.} = Po = (PI)g_c/(\rho_L d_{imp}^5\ \omega^3)$$

$$\rho_L = 1\ \text{g/cm}^3 = 62.4\ \text{lb/ft}^3$$

$$Po = 41{,}250(32.17)/(62.4)(0.987)^5(209.4)^3$$

$$Po = 0.00247$$

$$Sc = 1.707 \text{ (as before in I.A.)}$$

$$Kg(\text{lb/ft}^2\text{-hr}) = 3.9 \times 10^{-4} \frac{(0.074)(0.341)}{0.987} (1.258 \times 10^6)^{1.42} (1{,}345)^{-0.21}$$

$$\times (0.00248)^{0.4} (1.707)^{0.5}$$

$$= 119 \text{ lb/ft}^2\text{-hr}$$

or in terms of mole (28.8 lb air = 1.0 lb mole air),

$$Kg = 4.13 \text{ lb mol/ft}^2\text{-hr.}$$

Converting to cgs units $Kg = 4.13 \times (1.356 \times 10^{-4})$ g mol/cm^2-sec

$$\text{or} \quad Kg = 5.6 \times 10^{-4} \text{ g mol/cm}^2\text{-sec.}$$

II. LIQUID PHASE MASS TRANSFER COEFFICIENTS

A. Owens et al. (1964) using reaeration constant (Eq. 7)

$$K_2(\text{base e hr}^{-1}) = 50.5 \, v^{0.69}/h^{1.85}$$

for the clarifier weir

$$h = 1 \text{ cm}$$

$$v = Q/\text{x-sectional area of flow} = Q/\pi D \times h$$

$$= 0.07 \text{ m}^3/\text{sec} \times 10^6 \text{ cm}^3/\text{m}^3/\pi(1{,}940)(1) = 11.5 \text{ cm/sec}$$

$$K_2 = 50.5 \, (11.5)^{0.69}/(1)^{1.85} = 259 \text{ 1/hr}$$

The reaeration constant, K_2, is related to the liquid phase mass transfer coefficient as follows:

$$k_L(\text{g-mol/cm}^2\text{-sec}) = (h)K_2(\text{sec}^{-1})(\rho_L/MW_L)(D_{i\text{-}H_2O}/D_{O_2\text{-}H_2O})^{0.7}$$

$$= (1)(259/3{,}600)(1/18)(1 \times 10^{-5}/2.5 \times 10^{-5})^{0.7}$$

$$k_L = 2.11 \times 10^{-3} \text{ g-mol/cm}^2\text{-sec.}$$

Thus, the expression for k_L directly is

$$k_L = (50.5/3{,}600)(\rho_L/MW_L)(v^{0.69}/h^{0.85})(D_{i\text{-}H_2O}/D_{O_2\text{-}H_2O})^{0.7}$$

$$\text{or} \quad k_L = 7.79 \times 10^{-4}(v^{0.69}/h^{0.85})(D_{i\text{-}H_2O}/D_{O_2\text{-}H_2O})^{0.7}$$

B. Modified Owens et al., (Eq. C, Appendix A)

$$k_L(\text{lb-mol/ft}^2\text{-hr}) = 3.12(1.024)^{T-20}\ \nu_o^{0.67}(h/3)^{-0.85}\left(\frac{D_{i-H_2O}}{D_{O_2-H_2O}}\right)^{0.66}$$

$T = 25°C$

$D_{i-H_2O}/D_{O_2-H_2O} = 1/2.5 = 0.40$

$h = 240$ cm = 7.87 ft (for primary clarifier)

For windswept surface,

$\nu_o = U(\text{ft/sec}) \times 0.035$

$= 200$ cm/sec $(1/2.54 \times 12)) \times 0.035$

$= 0.23$ ft/sec;

then

$K_L = 3.12(1.024)^5(0.23)^{0.67}(2.623)^{-0.85}(0.40)^{0.66}$

$K_L = 0.315$ lb-mol/ft^2-hr

or $K_L = 4.28 \times 10^{-5}$ g mol/cm^2-sec.

For nonagitated regions,

$\nu_o = 0.1$ ft/sec

so that

$K_L = 3.12(1.024)^5(0.10)^{0.67}(2.263)^{-0.85}(0.40)^{0.66}$

$= 0.180$ lb mol/ft^2-hr

or $K_L = 2.45 \times 10^{-5}$ g mol/cm^2-sec.

C. Mackay and Yeun (1983) (Eq. 9, p. 22)

k_L' (m/sec) $= 10^{-6} + 0.0144\ U^{*2.2}\ Sc_L^{-0.5}$ for $U^* \leq 0.3$ m/sec

$= 10^{-6} + 0.00341\ U^*\ Sc_L^{-0.5}$ for $U^* > 0.3$ m/sec

where $U^* = (6.1 + 0.63(U_{10}))^{0.5}\ U_{10}/100$

with $U_{10} = 200 \text{ cm/sec} = 2 \text{ m/sec}$

$$U^* = (6.1 + 0.63(2))^{0.5}\, 2/100 = 0.0542 \text{ m/sec.}$$

Since $U^* < 0.3$ m/sec, the first equation is used.

$$Sc_L = \mu_{H_2O}/\rho_{H_2O}\, D_{i-H_2O} = 10^{-2}/1(10^{-5}) = 1{,}000$$

$$k'_L = 10^{-6} + 0.0144(0.0542)^{2.2}(1{,}000)^{-0.5} = 1.75 \times 10^{-6} \text{m/sec}$$

or

$$k_L = (k'_L \times 100)(\rho_L/MW_L) = 1.75 \times 10^{-4}(1/18)$$

$$k_L = 9.7 \times 10^{-6} \text{ g mol/cm}^2\text{-sec} .$$

For comparison purposes, k_L calculated by the second equation is as follows:

$$k'_L = 10^{-6} + 0.00341(0.0542)(1{,}000)^{-0.5}$$

$$= 6.8446 \times 10^{-6} \text{ m/sec}$$

$$k_L = 6.84 \times 10^{-4}/18 = 3.8 \times 10^{-5} \text{ g mol/cm}^2\text{-sec} .$$

D. Thibodeaux (1978) (Eq. B, Appendix A)

$$k_L(\text{lb mol/ft}^2\text{-hr})\; a_v V = \frac{J(POWR)(1.024)^{T-20°C}(\alpha)10^6}{165.04} \left(\frac{D_{i-H_2O}}{D_{O_2-H_2O}} \right)^{0.5}$$

where (POWR) = net agitator horsepower.

For the aeration basin,

$POWR = (PI) \times \text{eff.} = 75 \times 0.8 = 60$ Hp

$T = 25°C$

$\alpha = 0.85$, a constant

$J = 3$, a constant

$D_{i-H_2O}/D_{O_2-H_2O} = 0.4$

$a_v V$ = area of agitation = 96 m^2 = 96 x 10.76 = 1,033 ft^2.

$$k_L = \frac{3(60)(1.024)^5(0.85 \times 10^6)}{(165.04)(1{,}033)} (0.4)^{0.5} = 639 \text{ lb/mol/ft}^2\text{-hr}$$

$$k_L = 639(1.356 \times 10^{-4}) = 0.0867 \text{ g-mol/cm}^2\text{-sec} .$$

III. PROCESS SPECIFIC CALCULATIONS

In this section, the overall mass transfer coefficients and fractional removal calculations for each process are outlined. However, it is first instructive to derive the fractional removal equations that were presented in the text and subsequently used here. The fractional removal equations employed depends on the model used to describe the process. There are two different models that are employed for these calculations, the plug flow model, and the perfectly mixed reactor model.

In plug flow, there is no back or radial mixing in the liquid steam. Thus, ideally any differential segment can be thought of as a batch reactor with a reaction time equal to the residence time of the fluid in that reactor segment. Mathematically, this implies:

$$\tau = \int_{c_{in}}^{c_{out}} \frac{dc}{r} \qquad \text{III-1}$$

where τ = residence time, sec = V/Q;

r = rate of appearance, g mol/cm^3-sec;

c = concentration of desired species, g mol/cm^3;

V = reactor volume, m^3; and

Q = volumetric flow rate, m^3/sec.

The reaction rate, in the cases to be considered, is simply the evaporation or mass transfer rate as given below:

$$r = -K_{oL}\ aX \qquad \text{III-2}$$

where a = the surface area per volume, cm^2/cm^3;

K_{oL} = the overall mass transfer coefficient, g mol/cm^2-sec; and

X = the mole fraction of the desired species.

Note that we can express C in terms of X as follows:

$$C = (\rho_L/MW_L)X = \rho_L' X \qquad \text{III-3}$$

where MW_L = molecular weight of the waste stream g/g-mol total,

ρ_L = average density of the waste stream g/cm^3, and

ρ_L' = molar density = ρ_L/MW_L, g mol total/cm^3.

Then $dC = \rho_L' \, dX$, and substituting Equation III-2 into III-1 yields

$$V/Q = \int_{X_{in}}^{X_{out}} \frac{\rho_L' dX}{-K_{oL} aX} \qquad \text{III-4}$$

Assuming constant K_{oL} a and constant ρ_L', equation III-4 can be rearranged noting that aV = A (surface area) as follows:

$$-\frac{K_{oL}A}{Q\rho_L'} = \int_{X_{in}}^{X_{out}} \frac{dX}{X} .$$

Integrating and exponentiating yields:

$$X_{out}/X_{in} = \exp(-K_{OL}A/Q\rho_L').$$

Thus, the fraction of influent lost to the air is:

$$F_{air} = \frac{X_{in} - X_{out}}{X_{in}} = 1 - X_{out}/X_{in} = 1 - \exp(-K_{oL}A/Q\rho_L')$$

$$F_{air} = 1 - \exp(-K_{oL}A/Q\rho_L') . \qquad \text{III-5}$$

This equation is valid for all systems idealized as plug flow.

In a perfectly mixed reactor, there are no concentration gradients within the reactor or process vessel. Thus, the effluent concentration from the reactor is equal to the concentration within the reactor. A simple mole balance around the system, assuming steady-state operation, is:

Flow in - Flow out = loss by reaction.

$$Q(C_{in} - C_{out}) = -rV = K_{oL}(aV) X_{out}.$$

$$Q\rho_L'(X_{in} - X_{out}) = K_{oL} A X_{out}$$

or $$R_{air} = \frac{X_{in} - X_{out}}{X_{out}} = K_{oL}A/Q\rho'_L \qquad \text{III-6}$$

where R_{air} = ratio of loss (air emissions) to discharge.

Note that $R_{air} = \frac{X_{in} - X_{out}}{X_{out}} = \frac{X_{in}}{X_{out}} - 1$

or $$X_{out}/X_{in} = 1/(R_{air} + 1).$$

So that the fraction of influent lost the air is:

$$F_{air} = 1 - X_{out}/X_{in} = 1 - 1/(R_{air} + 1) = (1 + R_{air})/(1 + R_{air}) - 1/(1 + R_{air})$$

$$F_{air} = R_{air}/(1 + R_{air}). \qquad \text{III-7}$$

The denominator in Equation III-7 can be thought of as the sum of the ratios (the ratio of discharge to discharge must always be one). Other reaction terms can be included (e.g., biooxidation). Thus, in general,

$$F_{air} = R_{air}/\Sigma R . \qquad \text{III-8}$$

Other mechanisms are included in the reaction rate expression. For example, if biooxidation is included in the perfectly mixed reactor mass balance,

Flow in - Flow out = loss to air + loss by biooxidation

$$Q\rho'_L(X_{in} - X_{out}) = K_{oL}\ A\ X_{out} + B_i\ V\rho'_L\ X_{out}$$

$$\frac{X_{in} - X_{out}}{X_{out}} = \frac{K_{oL}A}{Q\rho'_L} + B_i(V/Q) = \frac{K_{oL}A}{Q\rho'_L} + \beta_i\tau$$

where B_i = Biological decay constant, $\sec^{-1}$.

Note that the ratio of air loss to mass discharged is still $R_{air} = \frac{K_{oL}A}{Q\rho'_L}$.

The ratio of biooxidation loss to the mass discharged is $R_{Biol} = \beta_i\tau$. Thus,

$$F_{air} = R_{air}/\Sigma R = R_{air}/(1 + R_{Biol} + R_{air}).$$

A. Pretreatment

For estimating Kg, the correlation of MacKay and Yeun is used. Thus, Kg $= 1.13 \times 10^{-5}$ g mol/cm^2-sec (refer to I.A.).

The correlation of Owens et al. (II-A) is used to estimate K_L.

For benzene in the pretreatment unit:

$$D_{i-H_2O}/D_{O_2-H_2O} = 0.4;$$

$$h = 3 \text{ m} = 300 \text{ cm}, A = \text{surface area} = 50 \text{ m}^2;$$

$$\nu = Q/\text{X-sec Area} = 0.07 \times 10^2/(50)^{0.5}(3) = 0.33 \text{ cm/sec};$$

$$K_L = 7.33 \times 10^{-4} (0.33)^{0.67}(300)^{-0.85}(0.4)^{0.7}$$

$$K_L = 1.44 \times 10^{-6} \text{ g mol/cm}^2\text{-sec}.$$

Using the partition coefficient for benzene, K = 305, the overall mass transfer coefficient is:

$$K_{OL} = (1/K_L + 1/(KKg))^{-1} = (1/1.44 \times 10^{-6} + 1/(305)(1.13 \times 10^{-5}))^{-1}$$

$$K_{OL} \approx 1.44 \times 10^{-6} \text{ g mol/cm}^2\text{-sec} .$$

Assuming plug flow through the pretreatment unit, Equation III-5 applies.

$$\begin{aligned} F_{air} &= 1 - \exp(-K_{OL}A/Q\rho_L') \\ &= 1 - \exp[-1.44 \times 10^{-6}(50)/(0.07 \times 100/18)] \\ &= 1 - 0.998 \\ F_{air} &= 0.0002. \end{aligned}$$

B. Clarifier

The entire volume of the clarifier will not be available for the flow of wastewater. Therefore, the stream depth is some fraction, f, of the clarifier depth. Letting h_d = clarifier depth (cm) and h_s = stream depth (cm), then h_d is related to h_s as follows:

$$h_s = fh_d .$$

Using the stream depth in the reaeration equation of Owens et al. (1964) (Eq. 8) yields:

$$K_2(\text{Kr}^{-1}) = 50.5\, \nu^{0.67}/(h_d{}^{1.85}f^{1.85}).$$

Converting to the liquid mass transfer coefficient as in sample calculations II.A:

$$K_L = (50.5/3{,}600)(1/18)\ h_d\ v^{0.67}/(h_d^{1.85} f^{1.85})\ .$$

Simplifying $k_L = 7.79 \times 10^{-4}\ (v^{0.67}/h_d^{0.85})(D_{i-H_2O}/D_{O_2-H_2O})^{0.7}\ f^{-1.85}$.

The inlet to the clarifier is near the center and below the surface by 30 cm or 1 foot. As the waste water travels to the periphery of the clarifier, the velocity of the stream decreases. The mass transfer coefficient is accordingly reduced. The velocity varies in proportion to the inverse of the radius, R_c.

$$V = Q(M^3/\mathrm{sec})/2\pi\ R_c\ f\ h_d)\ .$$

The time weighted average mass transfer coefficient can be obtained by integrating the function predicting the liquid phase mass transfer coefficient between the limits of the radius.

Thus, the average liquid phase mass transfer coefficient can be written as follows:

$$\bar{K}_L = \int_{r=o}^{r=R_c} \frac{K_L 2r dr}{R_c^2}\ .$$

Substituting for K_L, the following equation can be obtained:

$$\bar{K}_L = \int 7.79 \times 10^{-4} (D_{i-H_2O}/D_{O_2-H_2O})^{0.7}\ h_d^{-0.85}\ f^{-1.85}\ v^{.67}\ 2r\ R_c^{-2}\ dr\ .$$

Again substituting for the velocity as a function of the radius,

$$\bar{K}_L = \int 7.79 \times 10^{-4}\ (D_{i-H_2O}/D_{O_2-H_2O})^{0.7}\ h_d^{-0.85}\ f^{-1.85}$$

$$\times\ 2r\ R_c^{-2}\ {\frac{Q}{2\pi\ rf\ h_d}}^{.67}\ dr\ .$$

Separating constants from variables before integrating, the following expression can be obtained:

$$\bar{K}_L = 7.79 \times 10^{-4}(D_{i-H_2O}/D_{O_2-H_2O})^{0.7}\ h_d^{-1.52}\ f^{-2.52}$$

$$\times\ R_c^{-2}\ Q^{.67}(2)(.29189)\int_o^{R_c} r^{0.33}\ dr\ .$$

After integration,

$$\bar{K}_L\ =\ 4.54 \times 10^{-4}(D_{i-H_2O}/D_{O_2-H_2O})^{0.7}\ h_d^{-1.52}\ f^{-2.52}$$

$$\times\ R_c^{-2}Q^{0.67}\int_o^{R_c}\ \frac{r^{1.33}}{1.33}$$

Finally, $\bar{K}_L\ =\ 3.42 \times 10^{-4}(D_{i-H_2O}/D_{O_2-H_2O})^{0.7}\ h_d^{-1.52}\ f^{-2.52}(Q/R_c)^{0.67}$.

For benzene in the primary clarifier:

$D_{i-H_2O}/D_{O_2-H_2O}\ =\ 0.4.$

$h_d\ =\ 240$ cm

$Q\ =\ 0.07 \times 10^6\ \text{cm}^3/\text{sec}$.

$R_c\ =\ 1/2\ (19.4)(100) = 970$ cm.

Assuming $f\ =\ 0.1.$

then, $\bar{K}_L\ =\ 3.42 \times 10^{-4}(0.4)^{0.7}(240)^{-1.52}(0.1)^{-2.52}(70{,}000/970)^{0.67}$

$=\ 2.53 \times 10^{-4}$ g-mol/cm^2-sec.

The gas phase mass transfer coefficient is estimated from the correlation of Mackay and Yeun (1983).

$K_g\ =\ 1.13 \times 10^{-5}$ g/mol/cm^2-sec. (Sec. I, Part A).

Thus $K_{oL}\ =\ (1/\bar{K}_L + 1/(K\ K_g))^{-1} = (1/2.53 \times 10^{-4} + 1/(305)(1.13 \times 10^{-5}))^{-1}$

$=\ (4{,}243)^{-1} = 2.36 \times 10^{-4}$.

Assuming plug flow, Equation 30 applies so that

$X_{out}/X_{in}\ =\ \exp(-K_{oL}A/100\ Q\rho'_m)$

$=\ \exp -2.36 \times 10^{-4}(\pi(19.4)^2/4)/[(0.07)(100)/18]$

$=\ \exp(-0.179) = 0.8358$.

The fraction lost to the air is

$$F_{air} = 1 - X_{out}/X_{in} = 1 - 0.8358$$

$$F_{air} = 0.1642 .$$

C. Clarifier Waterfall

Estimate K_L using the correlation of Owens et al. (1964), but assuming 90 percent reduction since the turbulence in the freefalling waste stream is expected to be reduced. That is,

$$K_L = 0.10\ K_{LOwens} = 0.10(2.11 \times 10^{-3}) = 2.11 \times 10^{-4} \text{ g-mol/cm}^2\text{-sec.}$$

Again, the gas phase mass transfer coefficient is estimated by the correlation of MacKay and Yeun (1983).

$$K_g = 1.13 \times 10^{-5} \text{ g-mol/cm}^2\text{-sec (Refer to Section I, Part A).}$$

$$K_{oL} = (1/2.11 \times 10^{-4} + 1/(305)(1.13 \times 10^{-5}))^{-1}$$

$$= 2.0 \times 10^{-4} \text{ g-mol/cm}^2\text{-sec.}$$

Modeling the stream as plug flow, Equation 26 applies. Hence,

$$X_{out}/X_{in} = \exp(-K_{oL}A/Q\rho_m').$$

$$A = \pi DL = 1{,}940\ \pi(30) = 182{,}840 \text{ cm}^2.$$

$$Q = 70{,}000 \text{ cm}^3/\text{sec.}$$

$$X_{out}/X_{in} = \exp \frac{-2 \times 10^{-4}(182{,}840)}{70{,}000/18} = 0.99.$$

$$F_{air} = 1 - X_{out}/X_{in} = 0.01.$$

D. Equalization Basin

The model of MacKay and Yeun (1983) is used to estimate K_g. Thus, K_g = 1.13×10^{-5} g-mol/cm^2-sec (Refer to I.A.). The modified Owens' equation is used to estimate K_L. From Section II.B:

$$K_L = 0.717(1.356 \times 10^{-4})(h/3)^{-0.85}$$
(h in feet)

For the equalization basin, h = 3 m = 9.84 ft.

$$K_L = 3.54 \times 10^{-5} \text{ g-mol/cm}^2\text{-sec.}$$

Then,

$$K_{OL} = (1/3.54 \times 10^{-5} + 1/(305)(1.13 \times 10^{-5}))^{-1}$$
$$= 3.51 \times 10^{-5} \text{ g-mol/cm}^2\text{sec.}$$

Assuming the equalization basin to be well mixed, Equation III-6 applies.

$$R_{air} = 3.51 \times 10^{-5} (5{,}185)/(0.07 \times 100/18)$$

$$R_{air} = 0.468.$$

Assuming no biological activity, the fraction of influent emitted to the air is

$$F_{air} = R_{air}/(1 + R_{air}) = 0.468/1.468 = 0.3188.$$

E. Aeration Basin

1. Agitated Zones: Estimate K_L using the correlation of Thibodeaux (1978); estimate K_g using the correlation of Reinhart (1977).

$$K_{Lag} = 0.0867 \text{ g-mol/cm}^2\text{-sec.} \quad \text{(From Section II, Part D).}$$

$$K_{gag} = 5.6 \times 10^{-4} \text{ g-mol/cm}^2\text{-sec.} \quad \text{(From Section I, Part E).}$$

$$K_{OLag} = (1/0.0867 + 1/(305)(5.6 \times 10^{-4}))^{-1} = 0.0575 \text{ g-mol/cm}^2\text{-sec.}$$

2. Nonagitated Zones: Estimate K_L using the modified correlation of Owens et al. (1964); estimate K_g using the correlation of MacKay and Yeun (1983).

$$\nu = 0.1 \text{ ft/sec.}$$

$$h = 360 \text{ cm} = 360/(12 \times 2.54) = 11.81 \text{ ft.}$$

From Section II, Part B;

$$K_{Lnon\text{-}ag} = 3.12(1.356 \times 10^{-4})(1.024)^{T-20}\nu^{0.67}/(3.937)^{0.85}$$
$$\times (D_{i\text{-}H_2O}/D_{O_2\text{-}H_2O})^{0.66}$$

$$= 4.23 \times 10^{-4} (1.024)^{5}(0.1)^{0.67}(3.937)^{-0.85}(0.4)^{0.66}$$

$$K_{Lnon\text{-}ag} = 1.74 \times 10^{-5} \text{ g-mol/cm}^{2}\text{/sec}$$

From Section I, Part A

$$K_{gnon\text{-}ag} = 1.13 \times 10^{-5} \text{ g-mol/cm}^{2}\text{-sec}$$

then $K_{oLnon\text{-}ag} = (1/K_{Lnon\text{-}ag} + 1(KK_{gnon\text{-}ag}))\text{-}1$

$$= (1/1.74 \times 10^{-5} + 1/(305)(1.13 \times 10^{-5}))^{-1}$$

$$K_{oLnon\text{-}ag} = 1.73 \times 10^{-5} \text{ g-mol/cm}^{2}\text{-sec.}$$

The average overall mass transfer coefficient is calculated by weighting the agitated and nonagitated overall mass transfer coefficients by their respective surface areas.

The total surface area of the aeration basin is

$$A_{tot} = (170)(170) = 28{,}900 \text{ m}^{2}.$$

The surface area being agitated is:

A_{ag} = 96 (No. of agitators) = 96(30) = 2,880 m^2. Therefore, the nonagitated surface area is:

$$A_{non\text{-}ag} = A_{tot} - A_{ag} = 28{,}900 - 2{,}880 = 26{,}020 \text{ m}^{2}.$$

Thus, $\bar{K}_{oL} = (K_{oLag}\, A_{ag} + K_{oLnon\text{-}ag} A_{non\text{-}ag})/A_{tot}$

$$= [0.0575(2{,}880) + 1.73 \times 10^{-5}(26{,}020)]/28{,}900$$

$$= 5.75 \times 10^{-3} \text{ g-mol/cm}^{2}\text{-sec.}$$

The aeration basin is assumed to be well (perfectly) mixed. Consequently, the ratio of air emissions to discharge is given by Eq. 36.

$$R_{air} = \bar{K}_{oL}\, A_{tot}/(Q\rho'_{m} \times 100)$$

$$= (5.75 \times 10^{-3})(28{,}900)/(7/18) = 427.$$

The ratio of biological degradation to discharge is simply the biological decay rate constant times the residence time.

$$B_{i} = 1/400 \text{ hr} = 1/(400 \times 3{,}600) = 6.944 \times 10^{-7} \text{ sec}^{-1}$$

$$\tau = V/Q = (170)(170)(3.6)/(0.07) = 1.486 \times 10^{6} \text{ sec.}$$

So that

$$R_{bio} = B_i \tau = 1.032.$$

Since the ratio of discharge to discharge must be 1.0, the sum of the ratios is:

$$R_{tot} = R_{dis} + R_{bio} + R_{air} = 1 + 1.032 + 427$$

$$R_{tot} = 429.032.$$

Then, the fraction removed by the air is:

$$F_{air} = R_{air}/R_{tot} = 427/429.032 = 0.9953,$$

and the fraction removed by biological decay is:

$$F_{bio} = R_{bio}/R_{tot} = 1.032/429.032 = 0.0024.$$

F. Subsurface Aeration

It is assumed that the bubbles attain an equilibrium concentration based upon the thermodynamic partitioning of the VOCs into the gas phase. Thus the mass transfer of VOCs to the atmosphere includes both a surface diffusion and a bubble equilibrium term as given in Eq. 50.

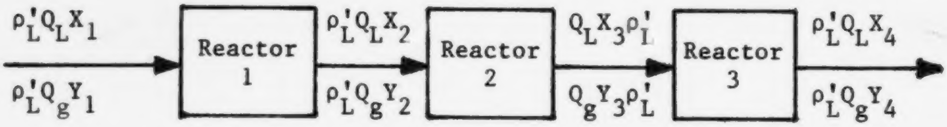
$$\text{Flux to air} = K_{OL} X_i + \rho'_g Q_g K X_i / A .$$

The overall mass transfer coefficient, K_{OL}, is estimated using the same correlations and averaging techniques as the surface aerated system when the subaeration basin is open to the atmosphere. If the subaeration basin is covered, then only mass transfer to the bubbles needs to be considered (i.e., the gas in the headspace is comprised solely of bubbles already assumed to be saturated with VOCs; hence no further emissions of VOCs to the gas in the headspace is possible).

For the closed UNOX system, $K_{OL} = 0$, so that only mass transfer to the bubbles needs to be considered. However, in the UNOX system, the waste stream is divided into four reactor trains consisting of three reactors per train. Fresh air is fed into the first reactor of each train only, and this gas is concurrently recirculated to the next two. Offgases of the third reactor are vented to the atmosphere.

It is assumed that the total liquid and gas flow is divided equally between the four trains. Consequently, each train has an identical fractional loss which is equivalent to the overall fractional loss of the system. This assumption permits modeling of the UNOX system of four trains as a single train that has reactors four times as large as the UNOX reactors.

Considering the system as one train:



Where Y_1 is the mole fraction of (for this example) benzene in the gas stream. We assume each reactor to be perfectly mixed so that the mole fraction of benzene in Reactor 1 is X_2, in Reactor 2 it is X_3, and in Reactor 3, it is X_4. We further assumed that the outlet gas of each is in equilibrium with the liquid in that reactor. Therefore, $Y_2 = KX_2$, $Y_3 = KX_3$, and $Y_4 = KX_4$. We assume $Y_1 = 0$. Also we assume that each reactor contains the same volume of liquid, and since Q_L remains constant through the train, each reactor has the same residence time, $\tau = V/Q_L$. (Note: This volume, V, is the actual volume of the reactors times the number of trains in the system.)

Making a mole balance on benzene around each reactor, and accounting for the biological oxidation rate, B_i, yields:

Flow in: liquid + gas = Flow out: liquid + gas + amt. biooxidation

Reactor 1 $\quad Q_L \rho_L' X_1 = Q_L \rho_L' X_2 + Q_g \rho_g' Y_2 + B_i \rho_L' X_2$

Noting that $\tau = V/Q_L$, $Y_1 = 0$, $Y_2 = KX_2$, and rearranging yields:

$$X_1 - X_2 = (Q_g \rho_g' / Q_L \rho_L')\ K(X_2 - 0) + B_i\ \tau X_2\ . \qquad \text{III F-1}$$

Since, for any one component in a train, $(Q_g \rho_g' / Q_L \rho_L')K$ and $B_i \tau$ remain constant, let

$$C = (Q_g \rho_g' / Q_L \rho_L')K \text{ and } D = B_i \tau.$$

Equation III F-1 becomes

$$\text{Reactor 1} \qquad X_1 - X_2 = CX_2 + DX_2\ . \qquad \text{III F-2}$$

Similarly, for Reactor 2 and 3,

Reactor 2 $$X_2 - X_3 = C(X_3 - X_2) + DX_3 \; ; \tag{III F-3}$$

Reactor 3 $$X_3 - X_4 = C(X_4 - X_3) + DX_4 \; . \tag{III F-4}$$

Adding Equations III F-2, III F-3, and III F-4 yields

$$X_1 - X_4 = CX_4 + D(X_2 + X_3 + X_4) \; . \tag{III F-5}$$

Solving Equations III F-3 for X_2 and III F-4 for X_3 yields

$$X_2 = X_3(1 + C + D)/(1 + C) \; ; \tag{III F-6}$$

$$X_3 = X_4(1 + C + D)/(1 + C) \; ; \tag{III F-7}$$

which implies $$X_2 = X_4(1 + C + D)^2/(1 + C)^2 \; . \tag{III F-8}$$

Substituting Equations III F-7 and III F-8 into Equation III F-5 gives:

$$X_1 - X_4 = CX_4 + DX_4(1 + (1 + C + D)/(1 + C) + (1 + C + D)^2/(1 + C)^2) \; .$$

Total loss = loss to air + loss by biooxidation.

The ratio of air emissions to discharge is

$$R_{air} = CX_4/X_4 = C = Q_g \rho'_g K/(Q_L \rho'_L) \; . \tag{III F-9}$$

Similarly, the ratio of biooxidative loss to discharge is:

$$\begin{aligned} R_{Biol} &= DX_4(1 + (1 + C + D)/(1 + C) + (1 + C + D)^2/(1 + C)^2)/X_4 \\ &= D(1 + (1 + C + D)/(1 + C) + (1 + C + D)^2/(1 + C)^2). \end{aligned} \tag{III F-10}$$

The series form of Equation III F-10 suggests that, in general, the ratio of biooxidation to discharge is:

$$R_{Biol} = D\,[(1 + C + D)/(1 + C)]^{n-1} \tag{III F-11}$$

where n = the number of reactors in series (i.e., the number of reactors in one train);

$D = B_i \tau$

and $C = Q_g \rho'_g K/(Q_L \rho'_L)$.

For the UNOX system, the overall liquid and gas flow rates are:

$$Q_L = 0.07\ \mathrm{m^3/sec} \qquad \rho'_L = 1/18\ \text{g-mol/cm}^3$$

$$Q_g = 0.40\ \mathrm{m^3/sec} \qquad \rho'_g = 1.185 \times 10^{-3}/28.8\ \text{g-mol/cm}^3.$$

Thus, for benzene, the ratio of air to discharge is:

$$R_{air} = C = Q_g \rho'_g K/(Q_L \rho'_L) = 0.4(1.185 \times 10^{-3})(305)(18)/(28.8 \times 0.07)$$

$$R_{air} = C = 1.291.$$

The biooxidation rate for benzene is $B_i = (1/400)(1/3{,}600) = 6.944 \times 10^{-7}$ sec^{-1}. The residence time, τ, is $\tau = V/Q = L \times W \times D \times \text{No. of trains}/Q$.

For the UNOX reactors L = 8.37 m, W = 8.4 m (Note: In Table 21, the length has already been corrected for the number of trains. L = 8.37 x 4 = 33.48 m). Thus, $\tau = 8.4 \times 33.5 \times 8.5/0.07$ or $\tau = 34{,}170$ sec. Then,

$$D = B_i\tau = 0.02373$$

$$1 + C = 2.291$$

$$1 + C + D = 2.3147 \ .$$

The ratio of biooxidation to discharge is:

$$R_{Biol} = 0.0237(1 + 2.3147/2.291 + (2.3147/2.291)^2)$$

$$= 0.0719.$$

$$R_{tot} = 1 + R_{air} + R_{Biol} = 1 + 1.291 + 0.0719 = 2.3629.$$

Therefore, the fractional losses are:

$$F_{air} = R_{air}/R_{tot} = 1.291/2.3629 = 0.5464 \ .$$

$$F_{Biol} = R_{Biol}/R_{tot} = 0.0719/2.3629 = 0.0304.$$

Appendix C

Estimation of Volatilization Rates Based on Changes in Concentration of a Reference Compound

APPENDIX C

ESTIMATION OF VOLATILIZATION RATES BASED ON CHANGES IN CONCENTRATION OF A REFERENCE COMPOUND

An approach suggested by OAQPS (Durham, 1985) involves prediction of volatilization rates of VOCs in the absence of other pathways based on the concentration profile of one reference compound as it moves through a series of unit operations. This approach could be used to indicate the presence of biooxidation or decomposition if observed concentration ratios deviated from predictions.

At steady state, assuming a perfectly mixed tank, the component balance for a wastewater containing two VOCs is:

$$QC_{f1} = QC_1 + E_1 + D_1 = QC_1 + K_{OL1}C_1A + D_1 \qquad (1)$$

$$QC_{f2} = QC_2 = E_2 + D_2 = QC_2 + K_{OL2}C_2A + D_2 \qquad (2)$$

where

A = surface area of treatment tanks, m^2

C = concentration in tanks, g/m^3

C_f = inlet concentration, g/m^3

D = decomposition rate, g/s

E = emission rate, g/s

Q = flow rate, m^3/s

K_{OL} = overall mass transfer coefficient, m/s.

Subscripts refer to compounds 1 and 2.

Rearranging and dividing Equation (1) by (2) gives

$$\frac{K_{OL1}C_1}{K_{OL2}C_2} = \frac{Q\ \Delta C_1 - D_1}{Q\ \Delta C_2 - D_2} \qquad (3)$$

where $\Delta C_1 = C_{f1} - C_1$ and $\Delta C_2 = C_{f2} - C_2$.

If no decomposition is taking place, then $D_1 = D_2 = 0$, and

$$\frac{C_1}{C_2} = \frac{K_{OL2}}{K_{OL1}} \frac{\Delta C_1}{\Delta C_2} . \qquad (4)$$

If the gas phase resistance is small relative to liquid phase resistance, then

$$\frac{K_{OL1}}{K_{OL2}} = \left(\frac{d_1}{d_2} \right)^{0.67} \text{, and} \tag{5}$$

$$\frac{C_1}{C_2} = \left(\frac{d_2}{d_1} \right)^{0.67} \frac{\Delta C_1}{\Delta C_2} \tag{6}$$

where d_1 and d_2 are the diffusivities of compounds 1 and 2 in water, cm^2/sec.

Individual pair of compounds can be analyzed according to Equation 50. If one of the compounds is not likely to decompose (e.g., $D_1 = 0$ in Equation (48), then D_2 can be calculated.

Though Equation (51) is theoretically sound in some cases, there were several assumptions made in its derivation that may limit its utility. First, process variations often cause significant changes in the concentrations of components in the influent stream, and consequently these variations invalidate the steady state component balances of Equations (46) and (47). Second, not all waste treatment units are perfectly mixed tanks so that the constant emission rate substitution (i.e., $E_1 = K_1C_1A$) used in Equations (46) and (47) are merely approximations. Third, the dependence of the overall mass transfer coefficients on the component diffusivities, as expressed in Equation (51), is not always correct. For surface agitated systems, the liquid phase mass transfer coefficient varies with the square root of the component diffusivity as seen by the correlation of Thibideaux (1978) (Equation B in Appendix A). For covered submerged aeration where the gas is in equilibrium with the liquid (as in the UNOX system), the overall mass transfer coefficient is independent of the component diffusivity (i.e., $K_{OL1}/K_{OL2} = K_1K_2$ where K_1 and K_2 are the partition coefficients). This, for steady-state, well-mixed process units, Equation (51) may still be inappropriate. In such as case, however, Equation (4) could be used and the overall mass transfer coefficient ratio could be calculated by applying the correct model for the specific process unit in question.

Besides the theoretical limitations of Equation (6), the analysis has several practical limitations. The foremost of these limitations are the inaccuracies of the chemical anlysis. If there is either a very large or a very small reduction in a component's concentration across a process unit, then C_i or ΔC_i, respectively, will approach zero. In such an instance, inaccuracies in the chemical analysis can have a large effect on the component ratios, and Equation (5) would incorrectly suggest the presence of alternative pathways. Inaccuracies also exist in the diffusivity data and mass transfer calculations.

Daily and average daily composite treatment process flows at the Union Carbide Plant were analyzed according to Equation (6) as follows:

$$R = \left(\frac{C_1}{C_2} \right) \frac{\Delta C_1}{\Delta C_1} = \left(\frac{d_2}{d_1} \right)^{0.67} = \frac{K_{OL2}}{K_{OL1}}$$

The term R as determined by the ratio of diffusivities or by the ratio of calculated overall mass transfer coefficients was in good agreement. These predicted values of R ranged from 0.8 to 1.1.

The term R as calculated by daily process flows varied widely (-1.4 to +110) due to process variations which caused large fluctuations in the component concentrations. The term R as calculated by the average flow data was much improved over the R calculated from daily flows (i.e., many R's $\cong 1$). However, for the aerated process units, large fluctuations in R persisted. These aerated process units exhibited large component reductions so that the chemical analysis error, not biooxidation, is thought to be responsible for the observed fluctuations.

Due to the theoretical limitations and the inherent inaccuracy of the chemical analysis and diffusivity data, Equation (6) has very limited applicability to industrial processes. However, Equation (6) may have some utility on a laboratory scale since the inherent assumptions can be more easily realized, and the component removal controlled so as to prevent C_i or ΔC_i from approaching zero.